ULTRAVIOLET AND CYCLOPOLYMERIZATION STUDIES OF NON-CONJUGATED DIENES

By

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DEDICATION

to my wife, mother and grandfather

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CHAPTER I

INTRODUCTION

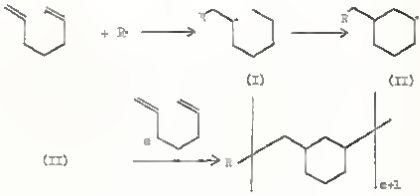
History of Cyclopolymerization

One of the most basic tenets of polymer chemistry concerns the polymerization of multifunctional monomers. Arising from the research of Staudinger and Heuer (1) in 1934, there grew the assumption that all monomers containing more than two reactive sites, would ultimately crosslink and gel. One would then expect monoolefins to yield soluble polymers, but di-, tri-, tetraolefins, etc. would yield insoluble, crosslinked polymers.

In 1951, Butler and Ingley (2) made a startling discovery while attempting to prepare polyquaternary ammonium salts suitable for ion-exchange resins. In agreement with theory, the tri- and tetraallylammonium salts gave water insoluble, crosslinked polymers. The corresponding diallylic compound behaved completely anomalously. It gave a water soluble polymer which showed no unsaturation. Under identical conditions the monoallylic compound did not polymerize.

In order to rationalize this unusual result, Butler (3) and Butler and Angelo (4) proposed an alternating intra-

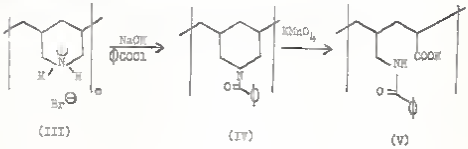
[illegible] mechanism (commonly referred to as the polymerization). The general form is depicted below.



An initiator reacts with one double bond producing an anion, cation or free radical (I). This intermediate then reacts, intramolecularly with the remaining double bond of the monomer to produce a new site now located on a ring (II). The reaction continues by attacking a new monomer molecule, etc. to yield a linear, saturated polymer containing cyclic repeating units. This mechanism does not intend to imply that the reaction is stepwise. To date, there is little evidence as to whether it is stepwise or a concerted reaction.

Proof for the polymer structure has been provided by research of Butler, Crawshaw and Miller (5). This work showed the presence of cyclic units in the polymer chain by

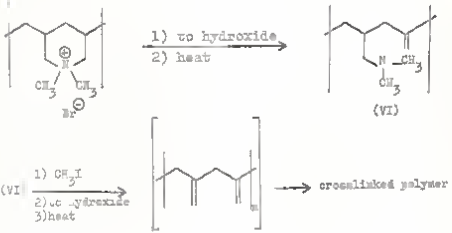
The following series of reactions in poly(diallyldimethylammonium chloride).



$$(V) \xrightarrow[\text{heat}]{} \text{crosslinked polymer} + \text{ØCOOH}$$

The polymer (III) was converted to the benzamide (IV) and then oxidized with potassium permanganate to (V). The structure of (V) was supported by elemental analysis, titration and infrared data. The conversion of (IV) to (V) exactly paralleled a similar conversion of N-benzoylpiperidine to N-benzoylvaleric acid (6). Upon strong heating, polymer (V) was found to eliminate benzoic acid and yield a crosslinked polymer.

Stronger evidence was furnished by the same authors by degradation of poly(diallyldimethylammonium bromide). The reaction sequence is outlined below.



(VII)

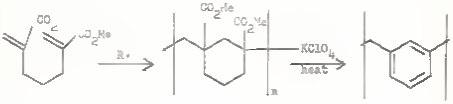
The polyquaternary ammonium salt was submitted to two Hofmann eliminations. The first elimination yielded (VI) which analyzed for 40 per cent unsaturation and nearly the theoretical amount of NMe_2 groups (as the methyl iodide derivative). Polymer (VII), resulting from a second pyrolysis, proved to be crosslinked and insoluble. The fact that (VI) did not lose a significant amount of nitrogen supports this mechanism.

Earlier investigators had established that cyclization did take place in certain polymerizations even though they led to insoluble polymers. Holt and Simpson (7) have shown that poly(diallyl phthalate) was 40 per cent cyclized. This agreed favorably with theoretical calculations (31%) of Haward (8). Later Oiwa and Ogata (9) found that diallyl phthalate could be cyclized up to 81 per cent under the proper conditions.

[illegible] experimental [illegible] presence of a six-membered [illegible] another possibility which must be considered [illegible] the five-membered ring (VIII). Evidence in favor of the six-membered ring was

(VIII)

presented by Carvel and Vest (10). These authors polymerized dimethyl α,α'-dimethylenepimelate (IX) by free radical initiation into a soluble polymer of high molecular weight (X). The polymer showed no unsaturation by infrared analysis.

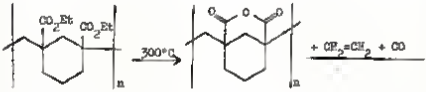


(IX) (X) (XI)

Dehydrogenation by potassium perchlorate at 390°C. yielded a new polymer containing aromatic rings. The presence of the benzene rings was established by the polymers infrared

absorption (1620, 1545 and 1500 cm.$^{-1}$) and its ultraviolet absorption (255mμ, 240mμ and below).

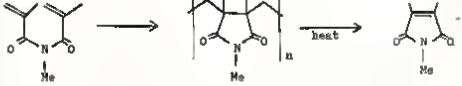
Further evidence was provided by experiments on the corresponding diethyl ester (XII). The polymer, when heated



(XII) (XIII)

to 300°C., lost ethylene and carbon monoxide and yielded a new polymer (XIII). (XIII) has infrared absorptions indicating it to be an anhydride.

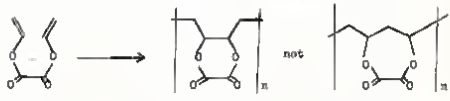
There recently appeared in the literature, evidence that at least some 1,6-diolefins polymerize to yield five or a mixture of five and six-membered rings. Goetzen and Schroeder (11) isolated N-methyl-2,3-dimethylsuccinimide (XIV) from the pyrolysis experiments on poly(N-methyl-methacrylimide). Koton et al. (12) have shown not only the



(XIV)

N-methyl but the N-ethyl, propyl and phenyl compounds behaved similarly. In contrast to these results, the authors found that methacrylimide polymerized to only six-membered rings. Sultanov and Arbuzova (13) have found that divinylacetals polymerize to mixtures of five- and six-membered rings in the ratio of 23 to 77. Somewhat similar results were found by Minoura and Mitoh (14).

Polymerization of 1,6-diolefins to five-membered rings represents a head to head reaction. Mark (15) had noted that some 1,7-diolefins cyclopolymerize in a similar manner (XIVb). Apparently the preference for a six-membered



(XIVb)

ring represents the driving force in this case.

Since the pioneering research on the polymerization of diallylammonium salts was reported, cyclopolymerization has been broadened and extended until it has encompassed nearly every conceivable combination of non-conjugated, diunsaturated molecule. No attempt will be made here to discuss or list every compound that is known to cyclopolymerize for this would be a monumental task in itself.

Instead, a few representative examples will be shown of various types of cyclopolymerization. Table 1 lists most of the monomers which have been cyclopolymerized from 1962 to mid-1966. A pre-1962 survey is available in the dissertation of M. Milne (16).

Cyclic polymers have been obtained from simple dienes such as 1,6-heptadiene by Marvel and Stille (17). Diacetylenic compounds have been shown to cyclopolymerize by Stille and Frey (18). Cyclic polymers can also be obtained from hetero atom containing monomers such as acrylic anhydride (19,20). Other examples are divinylacetal (21), diallyldimethylsilane (22,23), diallylphosphonium salts (24) and diallylphosphine oxides (25). The unsaturated linkages themselves may contain hetero atoms, for example, dialdehydes (26) and diisocyanates (27). The latter example may be depicted by the polymerization of propyleneisocyanate to a 1-nylon (28).

The scope of cyclopolymerization was further widened by the replacement of the double bonds by reactive rings.

[illegible]

NONOME[illegible]

[illegible]	[illegible]	Nonom[illegible]	[illegible]
[illegible]-[illegible],6-[illegible]tadiene	[illegible]	diallylace[illegible]	52
N-acrylsylacrylamide	[illegible]	α,α-diallylacetone	52
2-acrylsyloxyacrylates	[illegible]	diallylethanol	53
N-allylacrylamide	[illegible]	diallylformal	53
N-allylmethacrylamide	[illegible]	N,N-diallylformamide	44
allyl methacrylate	[illegible]	diallyl maleate	54
[illegible]-allylmethylenecyclohexane	[illegible]	N,N-diallyl-p-nitrobenzamide	44
[illegible]diene	[illegible]	diallylphenylacetonitrile	35
butylenediisocyanate	[illegible]	N,N-diallyl-N-phenylthiourea	44
[illegible]-carbocteoxy-N,N-dial[illegible]	[illegible]	diallyl phthalate	55
4-carbocthoxy-4-cyano-1,6-[illegible]tadiene	[illegible]	N,N-diallylurea	56
4-carbocthoxy-1,6-heptadiene	[illegible]	N,N'-diallylurea	56
4-carboxyl-1,6-heptadiene	[illegible]	α,α'-dichlorodiallyldimethylsilane	57
4-chloro-1,6-heptadiene	[illegible]	diethyl diallylmalonate	52
chlorourene	42	diethyleneglycol dimethacrylate	58
4-cyano-1,6-heptadiene	[illegible]	dimethallylamine	44
[illegible],2-cyclohexanediisocyanate	47	dimethyl diallylmalonate	45
1,3-[illegible]diisocyanate	48	5,7-dimethyl-1,6-octadiene	59
2-cyclohexyladipaldehyde	49	divinyl 2-alkoxybenzals	60
[illegible]-cyclopentanecarboxyl[illegible]de	50	divinyl alkylbenzals	61

[illegible]oldimethylmeth[illegible]	[illegible]	[illegible]enzal	62
[illegible]lacetamide	[illegible]	[illegible]yl benzene	63
[illegible]carbamates of gl[illegible]	[illegible]	[illegible]yl benzene diepox-	64
[illegible] carbonate	[illegible]	[illegible]-cyclohexadiene-4-acid chloride	35
[illegible] (R)(+)-3,7-dimethyl-[illegible]octanal	[illegible]	2,5-hexadiene diepoxide	29
[illegible]nyl formal and derivatives	62	4-hydroxy-1,6-heptadiene	35
[illegible]iryl furfural	68	2-hydroxysuberaldehyde	49
[illegible]vinyl isoamylal	21	isoprene	42
[illegible]vinyl isobutyral	21	malealdehyde	79
[illegible]vinyl methoxybenzals	69	methacrylic anhydride	80
[illegible]vinyl 4-methoxybutyral and and related compounds	70	methacrylic crotonic anhydride	81
[illegible],8-divinylnaphthalene	71	methacrylimide and derivatives	11,12
[illegible]vinyl oxalate	72	3-methoxysuberaldehyde	49
[illegible],2-divinyloxybutane	73	5-methylenenorbornene	82
[illegible]1-divinyloxycyclohexane	73	2-methylglutaraldehyde	83
[illegible]divinyloxypropane	73	2-methyl-1,5-hexadiene	84
[illegible]vinyloxypropanal	21	3-methyl-1,5-hexadiene	84
[illegible]vinylformal	74	monoallyl nitrocinnamates	85
[illegible]vinylacetoacetate	52	norbornadiene	85
[illegible],2-diisocyanate	47	1,5-octadiene	87
[illegible]-norbornadienecarboxylate	75	nonoallyl maleates	85
[illegible]ehyde	76	perfluoro-1,4-pentadiene	88

[illegible]	[illegible]	[illegible]	[illegible]
[illegible] onate	[illegible]	[illegible]phenylglutaraldehyde	[illegible]
[illegible] e	[illegible]	[illegible]henylglutaraldehyde	[illegible]
[illegible] isocyanate	28	1,[illegible]-propanediisocyante	47
[illegible] yde	90	propargylic anhydride	89
[illegible] hyde	91	trimethallylamine	44
[illegible] acetamide	92	trivinylphosphate	92
[illegible] tonitrile	92	vinyl allyl acetals	93
[illegible] ammonium hydrobromide	92	+-vinylcyclohexene	94
[illegible] lcarbinol	9[illegible]	vinyl ortheformate	92
[illegible] carbinol acetate	92	+-vinylmethylenecyclohexane	95
[illegible],3-tricyanatopropane	47	vinyl trans-cinnamate	96

[illegible] Watson ([illegible])

[illegible] has been shown to be applicable to [illegible] ring sizes [illegible]. In a classic study, [illegible] Garrison ([illegible]) have shown that α,ω-diolefins can be cyclopolymerized to soluble polymers with ring sizes varying [illegible] to twenty-one (Table 2).

[illegible]clopolymers have been made by all four known initiating systems (anionic, cationic, free radical and Ziegler). A particularly unique example is that of 2,6-diphenyl-1,6-[illegible]tone. This monomer was cyclopolymerized by each of [illegible] initiating techniques into soluble, cyclic polymers [illegible].

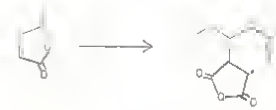
[illegible]ed cyclocopolymerization has been reported by [illegible]. Instead of forming the ring from one monomer, [illegible]tion incorporates two monomers. An example is [illegible]copolymerization of divinyl ether (a 1,4-diene) [illegible]ydride.

[illegible]

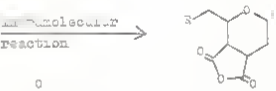
[illegible]

[illegible]	[illegible] size	[illegible] in [illegible] poly[illegible]	[illegible]	[illegible]soluble
[illegible]	7	25	[illegible]	2
[illegible]	[illegible]	9	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	41
[illegible]	[illegible]	[illegible]	[illegible]	40
[illegible]	[illegible]	[illegible]	[illegible]	36
[illegible]	[illegible]	[illegible]	[illegible]	32
[illegible]	[illegible]	[illegible]	[illegible]	57
[illegible]	[illegible]	[illegible]	[illegible]	22
[illegible]	[illegible]	[illegible]	[illegible]	37

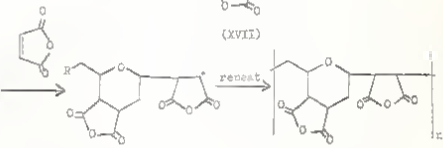
[illegible] (XVI)



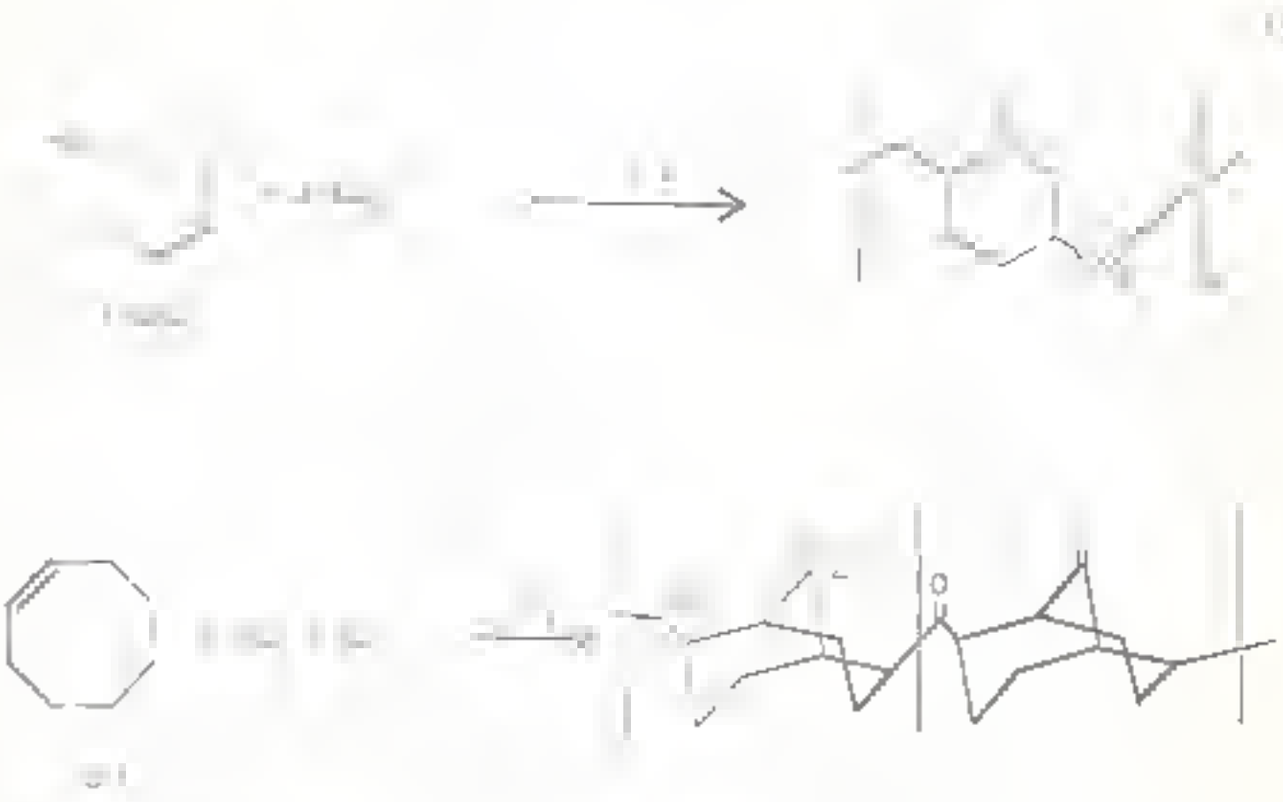
(XVI)



(XVII)



[illegible] 1,2-copolymers are of high molecular weight [illegible] organic solvents. Extension of [illegible] and a suitable second reactant may [illegible] the research of Stille and Thomson (33) [illegible] Frazier (34) on 1,5-cyclooctadiene



examples of cycloco-

cycloolymeriza-

structures and con-

are known today,

much to be done in

interactions

defined as two or

together by a single

et absorptions as

longer independent of

e, can be con-

[illegible] .RIZATION

[illegible]	[illegible]	Ref.
[illegible]	[illegible]	97
[illegible] ,4-pent[illegible]	[illegible]	98
[illegible] ,--pent[illegible]	[illegible]	98
[illegible]	[illegible]	99
[illegible]	[illegible]	100
[illegible]	[illegible]	99
[illegible]	[illegible]	100
[illegible]	[illegible]	101
[illegible]	[illegible]	102
[illegible]	[illegible] [illegible]	103
[illegible]	[illegible]	99
[illegible]	[illegible]	99

sidered to be composed of two ethylene-like systems. The main $\pi \rightarrow \pi^*$ absorption undergoes a bathochromic shift as can be seen in Table 4 (105,106). If, however, the chromophores are separated by insulating units, such as CH_2CH_2, then each unit should absorb independent of each other. This means that the effects of the absorbing groups should be additive. For example, the spectra of biallyl (1,5-hexadiene) corresponds very nearly to that of two propenes (104).

TABLE 4

ULTRAVIOLET ABSORPTIONS OF SOME POLYENES

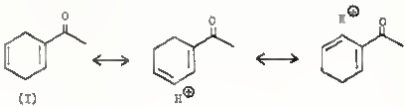
Name	Structure	λ_{max}	ϵ
ethylene	$CH_2=CH_2$	171	15,530
butadiene	$CH_2=CH-CH=CH_2$	217	21,000
hexatriene	$CH_2=CH-(CH=CH)-CH=CH_2$	258	35,000
octatetraene	$CH_2=CH-(CH=CH)_2-CH=CH_2$	296	52,000

This rule of additivity for non-conjugated chromophoric systems slowly began to break down as violations were found. Some of these violations are caused by what can be called non-conjugated chromophoric interactions. These effects have been defined by Jaffe (107, p. 437) as those

"which correspond neither to the simple addition of the spectra of the two insulated chromophores, nor to the spectra of the completely conjugated systems."

One of the earlier examples of non-conjugated interactions was from the work of Ramart-Lucas (108) and coworkers. She found that when n= 2 in systems such as $C_6H_5-(CH_2)_n-Y$ (Y=CN, CH=CH_2, COOH, etc.), the absorption was similar to that of an equimolar mixture of $C_6H_5CH_2CH_3$ and CH_3CH_2Y. However, when n=1, the intensities were somewhat enhanced although the wavelengths remained the same.

Braude and coworkers (109) found the $\pi \rightarrow \pi^*$ absorption in 2,5-dihydroacetophenon (I) was shifted bathochromically by 13 mμ from that of 1-acetylcyclohexene. The authors explained this shift by the hyperconjugative structures shown below. Braude (110) sought further evidence for hyperconjugation by studies on systems of the type XCH_2Y and XCH_2CH_2Y. He discussed and extended the work of Ley and Dirking (111) on X=Y=C_6H_5 compounds. The absorption of these compounds was similar to that of ethylbenzene and allylbenzene in the



(I)

aromatic region (260 mμ). They were quite different, however, in the 220 mμ region which the authors attributed to electronic interactions between the phenyl rings through hyperconjugation.

Kumler (112) investigated many α-phenylcarbonyl compounds such as α-phenylacetone and 2-methyl-2-phenylbutanone. He found that the $n \rightarrow \pi^*$ transition at 300 mμ was of unexpectedly high extinction values compared to the monophenylated materials. Hyperconjugation and enolization were ruled out by quaternary nature of the carbon containing the phenyl. Kumler concluded that there was a direct interaction of the aromatic ring and the carbonyl chromophore.

Within a few years, many examples of olefin-carbonyl interactions began to appear. In 1956, Bartlett and Tate (113) reported a bathochromic shift and an intensity enhancement for bicycloheptenone (II). The $n \rightarrow \pi^*$ absorption was shifted 13.5 mμ and had a tenfold increase in intensity over norcamphor (III). That same year, Cookson and Wariyar (114) investigated many unsaturated ketones and concluded that there was an increase in intensity when the p orbitals of C_1 and C_3, in the system $C^4=C^3-C^2-C^1=O$, pointed at one another.

(II)

(III)

(IV)

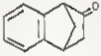
Caserio and Roberts (115) reported that 3-methylenecyclobutanone (IV) had a new peak at about 214 mμ. Leonard and Owens (116) found transannular interactions in trans-5-cyclodecenone (V) compared with cyclodecanone (VI). It is

(V)
260 mμ (423)
302 mμ (73)

(VI)
288 mμ (16)

(VII) 289.9 mμ (15)

interesting to note that the cis-5-cyclodecenone (VII) shows the typical, unenhanced n→π* absorption of the carbonyl group. Later, Koeower, Goering et al. (117) examined the far ultraviolet spectrum of the trans-unsaturated ketone and discovered a new transition at 214.5 mμ. Bartlett and Giddings (118) reported new transitions in 2-benzonorbornenone (IX) and 7-benzonorbornenone (X) at about 210 mμ plus enhancement of the carbonyl absorption.



(IX)

(X)

Ferguson (119) nicely summarizes this type of interaction in the following table.

TABLE 5

SUMMARY OF ULTRAVIOLET DATA FOR UNSATURATED KETONES

Type	Red shift with increasing polarity of solvent		Blue shift with increasing polarity of solvent	
	λ_{max}(mμ)	ϵ	λ_{max}(mμ)	ϵ
isolated C=O	185	10^3-10^4	280	50
	220-226	10^4	300-350	N50
transannular				
π-type	220-240	10^3	280-315	N50
homoconjugative				
σ-type	200-240	10^3	290-340	10^2-10^3

The new transitions occurring in the region 200-220 mμ can be seen at only slightly shorter wavelengths than the $\pi \rightarrow \pi^*$ transition in α,β-unsaturated ketones. Noting this, Labhart and Wagniere (120) reported on their LCAO-MO calculations on the coupling of an olefinic group with a carbonyl. The authors varied the resonance integral, β, from zero up to its value in α,β-unsaturated ketones and noted the change

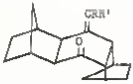
in the spectrum. From their calculations, Labhart and Wagniere predicted a new transition for a weakly coupled interaction in bicyclooctenone (XI) at 210 mμ. This agreed well with the experimental value of 202 mμ (121).

XI

(XI)

Winstein, Orloski and DeVries (122) have reported new transitions in the region of α,β-unsaturated ketones for the following compounds

solvent		R=R=H	R=H, R=CH_3	R=R=CH_3
heptane	λ_{max}(mμ)	209.5	219	239
	ε	3110	2720	3940
95% ethanol	λ_{max}(mμ)	214	224.5	244
	ε	1810	1455	2530



These authors noted that the interacting chromophores behaved similarly to α,β-unsaturated ketones. That is, replacement of hydrogen by methyl shifted the transition bathochromically as did the change to a more polar solvent.

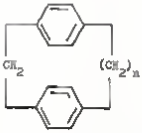
There are also instances of transannular interactions of heteroatoms and carbonyls. Georgian (123) and Marchant (124) have reported abnormal absorptions for (XII). The N-methyl compound absorbs at 232 mμ while Woodward's rules predicted absorption at 240 mμ. Leonard et al. (125) have reported transannular interactions in the spectrum of

(XII) (XIII) (XIV)

5-thiocyclooctane (XIII). A new transition was found at 226 mμ. The compound was also capable of being isolated as the bicyclic sulfonium salt (XIV) through treatment with perchloric acid.

There is slowly becoming available data on interactions in non-conjugated aromatic systems and non-conjugated diolefins. Bartlett and Lewis (126) observed, in 1950, that trypticene (XV) absorbed at about 8 mμ longer wavelength and three to five times the intensity of triphenylmethane. Cram and Antor (127) have noted abnormalities in the spectra of [1,n']-paracyclophanes (XVI) which the authors interpret as due to interactions between the phenyl rings.

(XV)



(XVI)

(XVII)

Zimmerman and Paufler (128) found new transitions at 203 and 239 mμ in the spectrum of barrelene (XVII). Winstein et al. (129) discovered new transitions in norbornadiene at 205, 214, 220 and 230 (sh) mμ. Hermann (130) has since reported the far ultraviolet spectrum of the same compound. He found an absorption at 183 mμ for the main $\pi \rightarrow \pi^*$ transition. Norbornene, the corresponding monoolefin, absorbs at 195 mμ. Extended molecular orbital calculations by both authors predicted absorptions at about 188 and 211 mμ. These calculations assumed an interaction in only the excited state. Story (131) reported in the same year on a new band at 214 mμ in the spectrum of 7-t-butoxynorbornadiene.

Analogous to his work on unsaturated ketones, Orloski (132) has also found evidence for a transannular interaction in the dimethylene compound (XVIII). Table 6 contains the data for (XVIII) and some other dienes that he investigated. On the basis of his results, Orloski interprets that an interaction has occurred. The molecular orbitals from the two chromophores have mixed producing two new absorptions,

TABLE 6

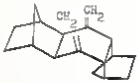
ULTRAVIOLET SPECTRA OF SOME UNSATURATED COMPOUNDS

Olefin	n-Heptane λ_{max}(mμ)(ε)		95 EtOH λ_{max}(mμ)(ε)		TFP[a] λ_{max}(mμ)(ε)	
	200	(7,950)				
	192 198	(13,900) (14,000)			186 194	(11,400)[b] (11,000)
	193	(8,400)	193	(8,630)		
	? peaks + sh.[c] 187 234	 (16,000) to (250) sh	6 peaks + sh. 188 (15,800) to 234 (226) sh			
	6 peaks + sh 192 242	 (8,850) to (237) sh	4 peaks + sh. 191 (9,700) to 242 (260) sh			
	187 206	(4,310)[b] (1,090) sh	188.3 (4,240)[b] 206 (1,040) sh			

a – 2,2,3,3-tetrafluoropropanol

b = not a maximum

c = shoulder



(XVIII)

one higher and one at lower energy than the original $\pi \rightarrow \pi^*$ transitions. These data seem to support his hypothesis.

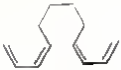
Recently, Woodward (133) has reported a strong end absorption at about 205 mμ in triquinanene (XIX). This might represent a new buried peak and hence, an interaction. Winstein and Radlick (134) have found shoulders at 200 and 212 mμ in the spectrum of cis, cis, cis-1,4,7-cyclononatriene (XX). Untch and Martin (135) have found a transition at 200 mμ in cis, cis,-cis-1,5,9-cyclododecatriene (XXI).

(XIX)

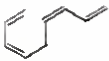
(XX)

(XXI)

Butler and Raymond (136) have published evidence for interactions between non-conjugated butadienyl systems as in 1,3,9,11-dodecatetraene (XXII) and 1,3,6,8-nonatetraene (XXIII).



(XXII)



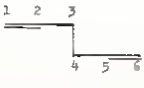
(XXIII)

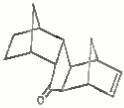
The latter compound exhibited a bathochromic shift of 11 mμ from 1,3-nonadiene besides a non-additive affect on the extinction coeffficients. This led the authors to propose an interaction between the two butadiene systems.

Iachie (137) has found evidence for interspecial interactions in the allylsilane series. By varying the substituents on silicon he was able to eliminate conjugation through the d-orbitals of silicon as the cause. Tetraallylsilane showed the greatest shift and was represented as.

The corresponding vinylsilanes do not show similar interactions.

There has also recently appeared another type of nonconjugated interaction involving 1,5-diunsaturated compounds with the 3,4-sigma bond at or near right angles to the unsaturations (138). Gookson calls these σ-coupled transitions. An example is the absorption of (XXIV) which absorbs at 224 mμ with an extinction coefficient of 1330.





(XXII)

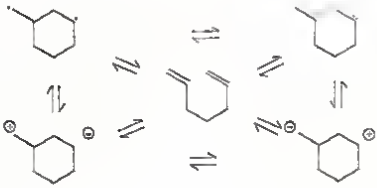
In summary it can be said that non-conjugated interactions are reasonably well established and that they give satisfactory answers to some puzzling anomalies in ultraviolet spectroscopy. As is usual in science, shortly after a rule is postulated, the exceptions appear as it has in the case of non-conjugated chromophores.

Development of the Problem

It has previously been mentioned that certain non-conjugated diunsaturated monomers can be polymerized into soluble, saturated polymers. The fact that many of these polymerizations can be performed on the neat liquid (bulk polymerization) to yield 100 per cent soluble polymers (16), seems to demand an explanation.

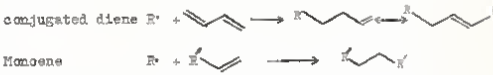
One of the earliest proposals was due to Butler (139, 140) in which he suggested that there may be an interaction between the two double bonds. This interaction can be interpreted as an excited state or ground excited state phenomena represented below. The interaction would render

polymerization through both double bonds the more favorable

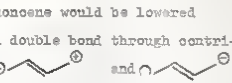


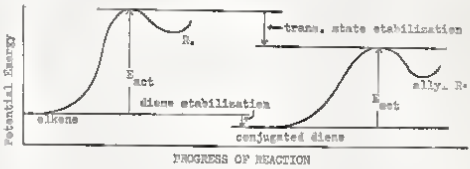
process versus polymerization through either double bond alone.

Presumably, a somewhat related polymerization is that of butadiene by a free radical source. Here both double bonds can interact with each other because they are joined by a sigma bond. Initiation by a radical, yields an intermediate which is resonance stabilized for the diene, but unstabilized for the monoene. This is represented below.



The effect of the second double bond would be to lower the energy of the intermediate radical from the diene relative to that of the monoene. This is represented above by the two approximately equal energy resonance forms that can be

drawn for the diene, but only the one form for the monoene. The ground state energy of the monoene would be lowered somewhat by addition of a second double bond through contributions of the resonance forms  and
However, these resonance forms are of significantly higher energy than that of the uncharged structure,
They will, therefore, contribute less to the stabilization of the ground state than the corresponding structures did to the transition state. The net result will be a lowering of the overall energetics for the conjugated diene relative to that of the monoene. This can be depicted by the potential energy diagram below (141).



These observations are supported by the fact that butadiene polymerizes predominantly by a 1,4-mechanism (142). The vinyl groups which escape polymerization in the polymer do not crosslink until high conversions are reached.

Extrapolation of these results to that of the non-conjugated diene is then attempted. The resonance inter-

action suggested by Butler would produce a lowering of energy for the cyclization step (or for the concerted reaction) yielding a saturated, cyclic polymer instead of a crosslinked resin.

If the theory is correct, evidence for these interactions may be available through ultraviolet spectroscopy. Using butadiene again as an example, its ultraviolet spectrum compared to ethylene is as follows.

compound	λ_{max} (mμ)	ϵ	ref.
$CH_2=CH_2$	171	15,530	(105)
$CH_2=CH-CH=CH_2$	217	20,900	(105)

A single double bond absorbs at 171 mμ. Placing a second double bond in conjugation with the first produces a bathochromic shift of 46 mμ and a somewhat less than doubling of the extinction coefficient. If the double bonds in Butler's models are interacting, its identification should be possible through ultraviolet absorption spectroscopy. A bathochromic shift, the appearance of a new transition or a disproportionate change in intensity on going from the monoene to the diolefin would signal that fact that an interaction was occurring.

The pattern for investigation would then be to synthesize suitable non-conjugated olefins, to investigate their ultraviolet spectra and to polymerize them. The spectra would be investigated for any anomalies fitting the

above criteria. The polymers would be analyzed to determine the per cent soluble and the amount of cyclization that has taken place. Then a correlation of these two investigations would be made to attempt the association of ultraviolet interactions with cyclopolymerization.

The first examination into this theory was made by Butler and Brooks (143). The authors synthesized cis and trans-1,3,8-nonatriene and other related olefins shown in Table 7. These compounds all show bathochromic shifts from

TABLE 7

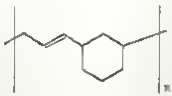
ABSORPTION OF SOME BUTADIENE DERIVATIVES

Compound	EtOH λ_{max} (mμ)	ε
myrcene	224.5	17,[illegible]
cis-1,3,8-nonatriene	225.4	20,300
trans-1,3,8-nonatriene	227	21,000
piperylene	223.5	23,000
isoprene	222	23,000

the 222 mμ predicted by Woodward's Rules (107, p. 136). It is also obvious that the ε values are not additive. An isolated double bond is essentially transparent in the 220-230 mμ region. The addition of the isolated third double bond should cause no change in the extinction coefficient which is seen not to be the case. Later work by Butler and Raymond (136) refutes the bathochromic shifts observed above

but supports the abnormalities in the ϵ value. These authors found that 1,3-nonadiene absorbed at 226.5 mμ (27,600).

Marvel and Hwa (144) found that myrcene could be polymerized by cationic catalysis into cyclic, soluble polymers. Other initiating systems yielded only the linear 1,4-polymer. Butler and Brooks found that the cis-nonatriene gave only insoluble polymer while the trans isomer did yield a 50 per cent soluble polymer. Structure (I) was assigned based on the solubility of the polymer and the infrared data.



(I)

Butler and Raymond (136) have investigated non-conjugated butadienyl systems. Table 8 summarizes their data. In all cases the ϵ values can be seen to be non-additive. The nonatetrene exhibits the largest bathochromic shift and also new absorptions at longer wavelength. This monomer, of the three studied, produced the poorest yield of polymer (145). The highest conversion obtained was 17 per cent of which only 10-50 per cent was soluble. The other tetraenes polymerized up to 50 per cent of which 50-75 per cent was soluble.

TABLE 8

ABSORPTION OF DIBUTADIENE DERIVATIVES

Compound	EtOH λ_{max} (mμ)	ε
1,3,9,11-dodecatetrene	228	41,[illegible]
1,3-dodecadiene	225.3	29,500
1,3,6,8-nonatetrene	237.1	32,400
	261.0	8,000
	272.1	5,500
1,3-nonadiene	226.5	27,500
3,6-dimethylene-1,7-octadiene	221.8	35,800
3-methylene-1-octene	224.7	20,400

Neither of the foregoing works conclusively established that interactions were occurring nor did they satisfactorily correlate with cyclopolymerization tendencies. It would seem more desirable to study less complicated systems such as non-conjugated diolefins. With the recent availability of instruments capable of searching the far ultraviolet, research into this area was now possible.

Diallyl (1,5-hexadiene) is known not to interact in ultraviolet (104) although it can be polymerized to cyclic polymers (146). Since the diene has many possible conformations not favorably aligned for interactions, it was thought

to be desirable to study other systems, specifically, systems which have greatly reduced modes of freedom, such as ring containing monomers. This restriction on the movements of the olefinic groups might increase to the likelihood of observing interactions in the ultraviolet. It is readily apparent from the history of ultraviolet interactions that only systems which are rigid or of limited flexibility have been found to exhibit anomalous spectra.

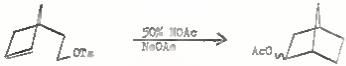
One series of compounds that were of interest was the unknown cis- and trans-1,3-cyclobutanes (II). In this system, geometric considerations should preclude the possi-

(IIa)

(IIb)

bility of interactions in the one isomer, while proximity of the olefinic linkages should aid the possibility of interaction in the other.

A second series of compounds was envisioned from the solvolytic cyclization studies of Bartlett (147), Clossen (148) and Winstein (149). Bartlett found that solvolysis of 4-cyclopentenylethyl tosylate (III) in acetic acid gave a product which was 92 per cent cyclic. Clossen found that

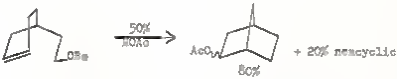


(III)

when the isomeric 3-cyclopentenyl brosylate (IV) was solvolyzed, no cyclic material was obtained. In a similar system, Winstein noted that 4-cyclohexenylethyl brosylate

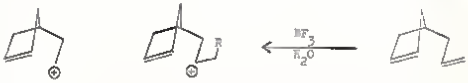
(IV)

(V) gave 80 per cent cyclic products.



(V)

Based on the ready cyclization tendencies of the compounds of Bartlett and Winstein, it was thought to be profitable to construct similar systems for polymerization. The work of Bartlett (150) has established that the reaction occurs by participation of the double bond during solvolysis. For deductive purposes only, intermediate (VI) can be con-



(VI) (VII) (VIII)

sidered the reaction intermediate. This ion can be closely approximated by ion (VII) which can be considered to form from the cationic initiation of polymerization of 4-allylcyclopentene (VIII). Similarly, the other solvolysed systems may be approximated by 4-allylcyclohexane (IX) and 3-allylcyclopentene (X). The unsynthesized 3-cyclohexenylethyl tosylate (XI) suggests the synthesis of 3-allylcyclohexene (XII).

The ready cyclization of the substituted ethyl tosylates suggests that the two double bonds may have a significant chance of interaction with one another and of yielding high percentages of cyclopolymers.

(IX) (X)

(XI) (XII)

Statement of the Problem

Based on the discussion in development of the problem, the proposed research may be stated as follows

1. to prepare suitable non-conjugated diolefins containing one carbocyclic ring. Specifically, 3- and 4-diallylcyclopentene, 3- and 4-diallylcyclohexene and cis- and trans-1,3-divinylcyclobutane are to be synthesized.

2. to study the ultraviolet absorption spectra of these monomers and any other available cyclic monomers which undergo cyclopolymerization.

3. to polymerize the above monomers and to characterize the resulting polymers in an attempt to determine their structure.

4. to attempt a correlation between unusual ultraviolet spectroscopic results of the monomer and the tendency of that monomer to undergo cyclopolymerization.

CHAPTER II

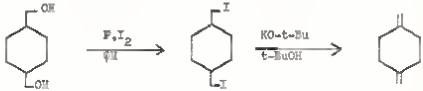
RESULTS AND DISCUSSION

Syntheses Related to Monomer Preparations

The syntheses relating to the contents of this dissertation may conveniently be considered in three categories. First, there was the synthesis of known 1,4-dimethylenecyclohexane and related compounds. The diolefin had been synthesized by Ball and Harwood (151) and was considered to be an interesting subject for ultraviolet analysis. The compound was also reported to cyclopolymerize.

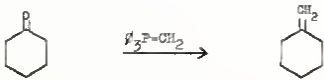
A second group of synthetic goals was the preparation of the diolefins suggested by the solvolytic ring closure experiments. The final area to be surveyed deals with the unsuccessful synthesis of the 1,3-divinylcyclobutanes.

The synthesis of 1,4-dimethylenecyclohexane by Ball and Harwood is outlined below. The commercially available



glycol was converted to the diiodide in 78 per cent yield. The diiodide easily cleaves with potassium tert-butoxide to the desired diolefin in 45 per cent yield. The presence of the exocyclic olefinic groupings was confirmed by infrared absorptions at 1785 cm.$^{-1}$ (CH_2=, overtone) and 890 cm.$^{-1}$ (CH_2= out of plane deformation). The absence of any absorption at 833 cm.$^{-1}$ eliminated the possibility of one or both double bonds migrating into the ring. The compound was found to be gas chromatographically pure.

The model compounds in this series were methylenecyclohexane and methylenecyclopentane. The former compound was synthesized by the well established Wittig reaction according to known procedures. Its experimental data are not included since the synthesis is quite routine.

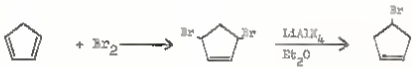


The procedure of Wittig (152) using butyllithium and tetrahydrofuran produced the olefin in a 21 per cent yield. Corey's (153) modification using sodium hydride in dimethylsulfoxide gave a much better yield of the olefin (59 per cent). Methylenecyclopentane and later quantities of methylenecyclohexane were purchased from commercial sources.

The syntheses of the four monomers suggested by solvolytic experiments are all similar since they involved

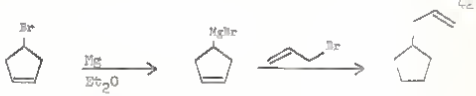
Grignard coupling reactions and unsaturated halocyclo-alkanes. Fortunately, each intermediate was a known and readily accessible material although not always in good yield.

Bartlett and Rice (154) reported in 1963, the synthesis of 4-bromocyclopentene. The reactions are outlined below.



Since the authors' publication, there have appeared several notices on the hazardous nature of this reaction (155). It has occasionally been noted that one hour after the completion of the addition of the dibromide to $LiAlH_4$, fires and/or violent explosions may occur. Unaware of any complications, this author had noted the onset of an exothermic reaction at this critical time. If the cooling bath used in the last step was not removed until the next day, the reaction proceeded without difficulties. The reaction was run successfully seven times with yields varying from 9-10.5 per cent.

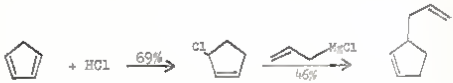
4-Allylcyclopentene was prepared by the coupling reaction of the Grignard reagent from 4-bromocyclopentene and allyl bromide. Unfavorable side reactions were minimized by filtration of the Grignard solution free of unreacted



magnesium. This eliminates the coupling of allyl bromide to 1,5-hexadiene (biallyl). The synthesis was straight forward and generally gave 30-38 per cent yields of 4-allylcyclopentene. Following the completion of this work, Bartlett et al. (156) reported the same synthesis. By inverse addition of the reagents, a yield of approximately 41 per cent can be obtained.

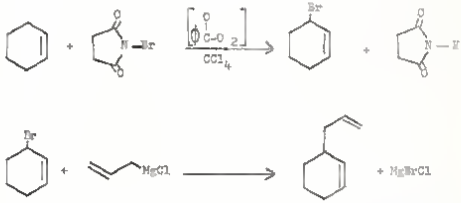
Evidence for the structure of 4-allylcyclopentene was supplied by its infrared spectrum. Absorptions at 3070, 2985, 1835, 1650, 992 and 912 $cm.^{-1}$ confirmed the presence of the vinyl group. The cis double bond was shown to be present by absorptions at 1620 and 670 $cm.^{-1}$. Near infrared data (157) also confirmed these findings (1.633 and 2.115 μ, vinyl; 2.138 μ, cis double bond). Nuclear magnetic resonance (NMR) exhibited absorptions at 4.43 (CH=), 4.97 and 5.19 τ (CH_2=). The integrated ratio of areas of sp^2 to sp^3 hydrogens (5:7.35) was in good agreement with theory (5:7).

The isomeric 3-allylcyclopentene was prepared from known 3-chlorocyclopentene by the following sequence of reactions.



Hydrogen chloride gas was added to freshly cracked cyclopentadiene following the procedure of Noller and Adams (158). The distilled unsaturated chloride was then coupled with allylmagnesium chloride prepared according to the method of Kharasch and Reinmuth (159). The structure of 3-allylcyclopentene was confirmed by its infrared, near infrared and NMR spectra. The NMR $sp^2:sp^3$ hydrogen ratio of 5:6.97 was in excellent agreement with theoretical ratio of 5:7.

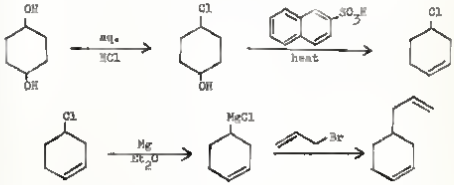
3-Allylcyclohexene was synthesized by the following procedure.



Cyclohexene was brominated by the method of Bailey and Nicholas (160) generally in yields of 55-65 per cent. The

resulting 3-bromocyclohexene was coupled with allylmagnesium chloride to yield 3-allylcyclohexene in yields of 56 to 72 per cent. The structure of the diolefin was supported by its infrared, near infrared and NMR spectra. The NMR determined $sp^2:sp^3$ hydrogen ratio of 5:8.9 was in good agreement with the theoretical 5:9.

4-Allylcyclohexene was synthesized as follows:



A cis, trans mixture of cyclohexane-1,4-diol was converted to the chlorohydrin in 62 per cent yield by the method of Owen and Robins (161). Gas chromatography revealed the presence of eight components. Two of the peaks totaled 75 per cent of the area and presumably represented the cis and trans halohydrin. The crude chloroalcohol was dehydrated in 220°C. bath according to the procedure of Biroh, Dean and Hunter (162). The maximum yield was 65 per cent. Gas chromatographic analysis revealed the product to be 99 per

cent pure. The chlorocyclohexene was carried [illegible] to produce 4-allylcyclohexene in 60 per cent [illegible]. The presence of allylic and cis double bonds were confirmed by infrared, near infrared and NMR spectra. The NMR sp^2:sp^3 hydrogen ratio (5:10.5) was in fair agreement with theory (5:9).

Two compounds were needed as models for the ultraviolet spectral studies. These were allylcyclohexane and 3-propylcyclohexene. Allylcyclohexane was synthesized by the coupling of cyclohexylmagnesium bromide and allyl bromide through a modification of the procedure of Rasseguier (163). Its structure was confirmed by infrared and NMR spectra. The sp^2:sp^3 hydrogen ratio of 3:12.8 was in good agreement with theory (3:13).

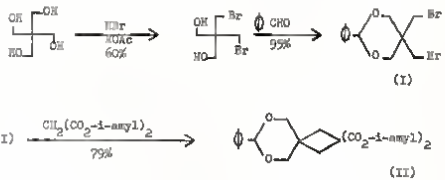
3-Propylcyclohexene was synthesized by the coupling of 3-bromocyclohexene and propyl bromide following the procedure of Berlande (164). The yield of product was about 50 per cent. Careful fractionation yielded a sample pure by infrared and NMR spectra. The sp^2:sp^3 hydrogen ratio of 1:7.09 agrees with the theoretical 1:7. Elemental analysis, however, revealed a total carbon, hydrogen content of only 97.6 per cent. Gas chromatography confirmed the presence of a small amount of impurity.

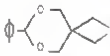
The impurity was found to be 3-bromocyclohexene based on a rapid silver bromide precipitate when the olefin

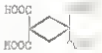
was shaken with alcoholic silver nitrate. The bulk of the olefin was stirred with aqueous silver nitrate and then chromatographed over alumina to remove the end product, 3-cyclohexanol. Redistillation produced a fraction which contained less than one per cent impurity by gas chromatography. Elemental analysis indicated a carbon, hydrogen total of 99.9 per cent.

The final series of syntheses to be discussed are those leading to the preparation of 1,3-divinylcyclobutane. Unfortunately there was not time to finish this lengthy synthesis and so it will be discussed briefly.

The proposed synthesis was based on the intermediate 1,3-cyclobutanedicarboxylic acid synthesized by Deutsch and Buckman (165). The sequence of reactions is outlined below. Only one reaction deserves special mention.



(II) $\xrightarrow[\text{2) HCl 97\%}]{\text{1) KOH}}$ 

(III) $\xrightarrow[\text{2) fuming HNO}_3\ 75\%]{\text{1) 2N-HNO}_3}$ 

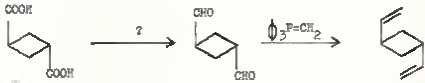
(IV) $\xrightarrow{\text{CH}_3\text{COCl}}$ +

45% 50%

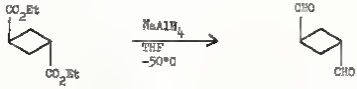
The over all 30 per cent yield sequence suffered the b[illegible] loss in the conversion of (III) to (IV). The temperat[illegible] of the reaction turned out to be quite critical. If [illegible] oxidation was run between 40-50°C, yields in the vicinity of 50-70 per cent could be attained regularly. If [illegible] action was attempted at higher temperatures, the yield dropped rapidly to zero. Deutsch and Buckma[illegible] do not mention this. These authors also claimed an 88 per cent yield for the same reaction. Interestingly, the tetrac[illegible] (I[illegible]) is

stable to refluxing nitric acid so some intermediate must be very sensitive to the reaction conditions.

The proposed route to 1,3-divinylcyclobutane was through the dialdehyde.

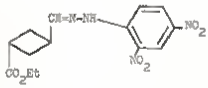


Six methods which customarily give aldehydes by oxidation of the ditosylate or glycol failed in this case. The only successful method found was that of Zakharkin et al. (166). This method involved the low temperature reduction of the diester with sodiumaluminumhydride.



The main difficulty was that the reaction did not give pure dialdehyde and the subsequent purification was not achieved. The trans isomer seemed to give mainly the mono-aldehyde while the cis isomer did give a reasonable amount of the dialdehyde. The purest fraction on distillation appeared

o contain three ester groups to one aldehyde grouping as deduced from NMR. The mono aldehyde was successfully analyzed as the dinitrophenylhydrazone (V).



(V)

Wittig reactions on the purest fractions of the cis or trans dialdehydes did not yield any identifiable olefinic products. The precise laboratory details and further comments may be found in the experimental section.

Ultraviolet Spectra of the Monomers

The ultraviolet light absorption of a molecule measures the energy necessary to promote an electron from the ground state to an excited state. The energy difference between these two states is equal to the following relationship:

$$\Delta E = E_{E.S.} - E_{G.S.} = h\nu = hc/\lambda$$

Where E is the energy of the state in question, h is Planck's constant, c is the speed of light and λ (lambda) is the value of the wavelength of light corresponding to

this energy difference. It is seen that the energy difference is inversely proportional to the wavelength of absorption.

The electrons in organic systems can be represented as either σ (sigma), π (pi) or n (nonbonding) electrons, depending on the type of bonding or nonbonding the component orbitals undergo. There are also antibonding orbitals to be considered; σ^* (sigma antibonding) and π^* (pi antibonding). Their relative energies are shown below.

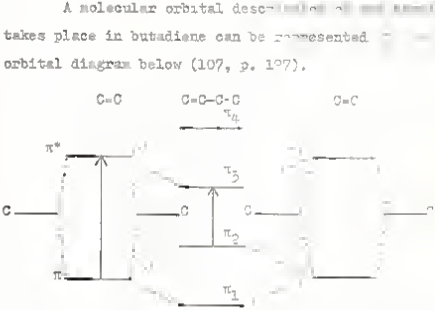
Since the olefin systems under discussion have no nonbonding electrons, they will not concern us here.

The ultraviolet absorption of olefins represents the excitation of an electron in the highest energy, occupied orbital to the lowest unoccupied orbital. These orbitals are, respectively, the π and π^* orbitals. The ultraviolet absorption is then referred to as a $\pi \longrightarrow \pi^*$ transition.

Non-conjugated diolefins, such as ethylene, generally absorb in the region of 170-200 mμ depending on the substitution pattern, geometry of the double bond, etc. These wavelengths correspond to 168 and 142 Kcal. per mole.

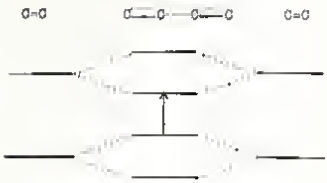
respectively. Conjugated d[illegible] in the region from 217 to 29[illegible] tution, geometry, etc. The [illegible] 99 Kcal./mole.

A molecular orbital desc[illegible] takes place in butadiene can be represented [illegible] lecular orbital diagram below (107, p. 1[illegible]).



The bathochromic shift observed for the conjuga[illegible] diene results from a mixing of the π orbitals of the isolated C=C groups. The lowest unoccupied orbitals and the highest occupied orbitals, π_3 and π_2, are seen to have been moved closer together, thus decreasing their energy difference.

In a system containing two olefinic groupings, not formally conjugated, a similar energy diagram can be constructed.



Depending on such factors as the amount and geometry of overlap of the π electron systems, a somewhat similar situation to that in butadiene should exist (111). The energy of the resultant transition should be inversely proportional to the amount of overlap in the first approximation (167). Consequently, as interaction occurs, it would be expected that the absorption maximum would shift to longer wavelengths.

This reasoning leads one to postulate bathochromic shifts or new, longer wavelength absorption bands as evidenced for interactions. It also seems reasonable that if there were no interaction, the intensities of the component parts of the diolefin should be exactly double that in the monoolefin. Any deviation from the expected intensity might be evidence for interaction. It must be pointed out, however, that the experimental ε value is quite susceptible to procedural errors and also to stray light errors in the far ultraviolet (168). Due concern must be shown for any

small abnormalities since they may reflect only [illegible]-mental error.

The effect of solvents on the $\pi \rightarrow \pi^*$ transition [illegible] olefins is a well recognized but poorly understood phenom[illegible]. A concise summary of the problem is contained in the cl[illegible] book on ultraviolet spectroscopy by Jaffe and Orchin. [illegible] effects are of importance in this study. First, nonpol[illegible] solvents produce spectra which closely resemble that of [illegible] vapor. In such solvents as heptane and isooctane, vapor-[illegible] fine structure is visible as it is in the vapor spectr[illegible]. More polar solvents tend to dampen the vibrations of [illegible] solute through solvation. Such solvents as acetonitrile and ethanol will produce in many cases spectra free of vibrational peaks.

A second effect of solvent polarity is shown on the maxima. In systems such as C=C and C=O, the excited state can be represented by large contributions from highly polar structures like $\overset{\oplus}{C}-\overset{\ominus}{C}$ and $\overset{\oplus}{C}-\overset{\ominus}{O}$. Polar solvents facilitate the electronic excitation by solvation of the excited state more than that of the ground state. Thus bathochromic shifts are found on changing solvent polarity from the least polar to the more polar.

The ultraviolet spectra of 1,4-dimethylenecyclohexane, methylenecyclohexane and methylenecyclopentane are listed in Table 9. Methylenecyclohexane was selected as the

ULTRAVIOLET SPECTRA 1,4-DIMETHYLENECYCLOHEXANE [illegible]

Compound	Solvent	λ_{max} (mμ)	ϵ
	isooctane	198.2 202.8 (sh) 208.6 (sh)	21,000 18,500 10,300
	95 % ethanol	198.6 203.3 (sh) 208.9 (sh)	19,500 17,200 9,000
	isooctane	191.3 197.5 (sh	11,700 9,200
	95 % ethanol	190.8	10,800
	n-heptane	195.4	8,800
	95 % ethanol	195.3	7,700

closest possible [illegible] ring analog was investigated to determine [illegible] strain on the absorption.

1,4-Dimethylenecyclohexane exhibited [illegible] 198.2 mμ and two longer wavelength shoulders [illegible] mately 203 and 208.5 mμ (isooctane). Figure [illegible] experimentally determined curve. This diene [illegible] expected small bathochromic shift on going to [illegible] polar solvent, 95 per cent ethanol. The [illegible] also caused a decrease in intensity of the absorption, [illegible] was a general phenomena with all the olefins [illegible] monomers were found to obey Beer's Law (absorption proportional to concentration).

It seems clear that increasing ring strain causes the absorption to longer wavelengths. [illegible]ethylenecyclohexane absorbs at 191 mμ while the five-membered ring analogue absorbs at 195 mμ. Introduction of a second sp^2 carbon into the six-membered ring, as in 1,4-dimethylenecyclohexane, probably is the reason for the shift to 198 mμ.

The shoulder present in the six-membered ring olefins presents a problem in interpretation. The removal of the shoulder in methylenecyclohexene by a polar solvent suggests the blurring out of a vibrational band. If this were so, it would be necessary to ascertain whether two

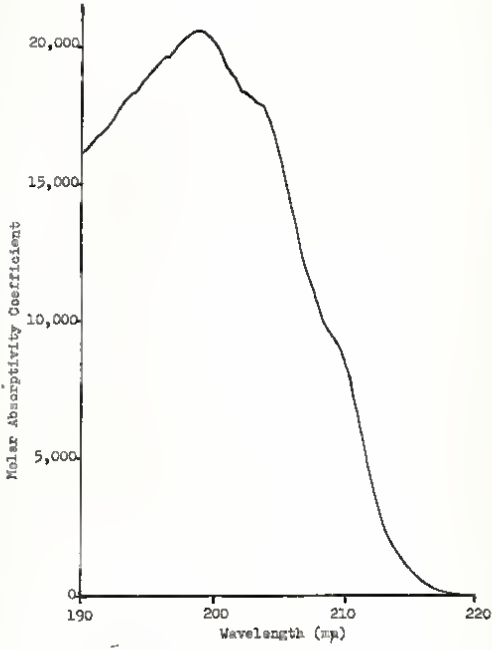


Fig. 1.-Absorption curve of 1,4-dimethylenecyclohexane in isooctane.

electronic transitions [illegible] in the ground electronic [illegible] vibrational levels in the [illegible] An alternative explanation [illegible] lowest lying vibrational [illegible] state to the excited [illegible] electronic excited state.

Evidence which [illegible] bilities or suggests some other cause for [illegible] shoulders was not available. [illegible] usually [illegible] electronic transitions occur from the ground vibrational state since at room temperature a preponderance of [illegible] molecules are in that state (107, p. 135). A crude [illegible] calculation was made to determine the energy [illegible] by the difference between the λ_{max} and the approximate position of the first shoulder. The difference of [illegible] was comparable to the C=O vibrational stretching [illegible] in the infrared. However, a Boltzmann distribution $\left[\frac{n_1}{n_{2ee}}\right]^{-(e_1-e_2)/kt}$ indicated that for this energy difference only 34 out of 10,000 molecules would be in this excited vibrational state. This was inconsistent with the magnitude of the shoulder, even after subtracting out the [illegible] absorption.

A careful consideration of the v[illegible] benzene reveals that they were symmetr[illegible] about the envelope (107, p. 244). Inve[illegible] high energy side of the $\pi \rightarrow \pi^*$ band in [illegible] was obscured because of the onset of ion[illegible] Hence, the correlation with the vibrat[illegible] benzene was impossible.

A conclusion must be reached [illegible] the shoulder in methylenecyclohexane [illegible] the present date. A temperature st[illegible] and computer [illegible] of the absorption curves would be helpful.

There was double the problem in 1,4-dimethy[illegible] cyclohexane due to the presence of the two shoulder[illegible] Again assignment of the shoulders to a particular [illegible] impossible. The energy separation between the vibr[illegible] in the region of 1200 cm.$^{-1}$. A Boltzmann distribu[illegible] cated a low population for excited vibrational sta[illegible] the ground electronic state (0.0013). A second vib[illegible] level should be even more sparsely populated. [illegible] difficult to determine if the long wavelength sho[illegible] could arise from this low population. The high e[illegible] of the absorption peak was also obscured by ionization processes.

It must be again concluded that without further investigation, a definite assignment could not [illegible]

There was the possibil[illegible] between the double bonds [illegible] transition. The fact [illegible] possibly indicate that [illegible] in several conformations [illegible] ferent magnitudes were [illegible] be c[illegible] as speculation since no [illegible] were [illegible].

A temperature study was attempted on the mono[illegible] NMR spectroscopy. The diolefin was studied as the pe[illegible] liquid over a temperature range from 25°C to -40°C ([illegible] ing point). No evidence of peak broadening or [illegible] was found.

Simple Huckel molecular orbital calculations [illegible] performed on the diolefin (see Appendix). The molecule was assumed to be in the boat conformation (I) and [illegible] normal bond lengths and angles. Calculations indica[illegible]

(I)

that the bow-stern distance of the ring was 2.58 [illegible]. [illegible] actual M.O. calculations were executed in accordance [illegible] the procedure outlined by Roberts (169). Extrapola[illegible] sigma, sigma and pi, pi overlap integrals from [illegible] (170) were used for the nonorthogonal orbitals.

A value of 0.48 β was obtained for the resonance integral between the olefinic groups. Using this value, the following energy diagram was obtained through the use of the standard M.O. calculating procedure:

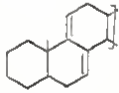
____ α - 1.27 β

____ α - 0.79 β

xx α + 0.79 β

xx α + 1.27 β

This value of β indicated a delocalization energy of 0.11 β for the non-conjugated diolefin. This is to be compared with the delocalization energy of butadiene (0.47 β). A delocalization energy which is 24 per cent that of butadiene seems large. If Woodward's rules are used loosely and applied to this system, a calculated λ_{max} of 245 mμ is obtained. A somewhat similar system (II) also absorbs at 245 mμ (107, p. 200).

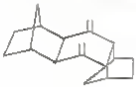


(II)

A transition representing 24 per cent of the delocalization energy of butadiene would be expected to occur at 207 mμ (0.24 x 50 mμ) using methylenecyclopentane as the model. This calculation assumes that a linear relation ship exists between λ_{max} and the delocalization energy. The result

[illegible]
probably fortuitous.

As mentioned [illegible]
the analogous system [illegible]
system (III) was looked into [illegible] conformations,



(III)

[illegible]

Figure 2 reproduces Orloski's [illegible]
mono and diene. These data were [illegible]
from non-conjugated interactions [illegible]
It was noticed that the diole [illegible]
tensity at longer wavelengths than [illegible]
was interpreted as being caused [illegible]
about 210 mμ which was submerged [illegible]
tion at 200 mμ. The transition at 198 mμ [illegible]
to a new absorption.

Orloski also found new transitions in [illegible]
(IV) and (V) listed in Table 5 (Chapter 1).

(IV)

(V)

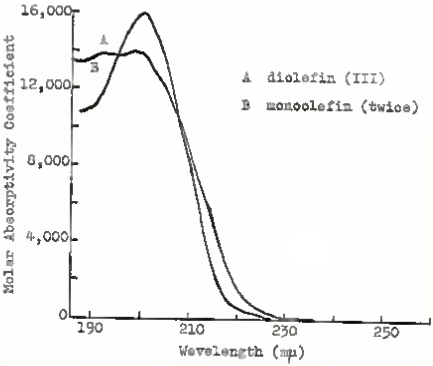


Fig. 2.-Ultraviolet absorption spectra of (III) and the corresponding monoolefin.

Aside from several [illegible] exhibited a new band [illegible] shorter wavelength [illegible] longer wavelength than that of the [illegible]. The data for the new transitions are l[illegible]

compound	new short wavelength band	old $\pi \rightarrow \pi^*$ band	[illegible]
(III)	192	1[illegible]	[illegible]
(IV)	187	1[illegible]	[illegible]
(V)	192	19[illegible]	[illegible]

Orloski concludes that the interaction be[illegible] olefinic groups has produced a higher and a lo[illegible] transition. The lower energy absorption is simil[illegible] $\pi_2 \rightarrow \pi_3$ transition in butadiene.

Evidence for a new high energy band could [illegible] found in the spectra of 1,4-dimethylenecyclohexane, [illegible] it is assumed that the main transition corres[illegible] first shoulder. This does not seem likely.

The evidence indicates that an interaction [illegible] occurring in 1,4-dimethylenecyclohexane. Possi[illegible] work, coupled with that of Orloski, establishe[illegible] conjugated diolefins can have overlap of their [illegible] systems to produce transitions similar to those [illegible] and other conjugated systems.

A second series of investigations dea[illegible] isomeric 3- and 4-allylcyclo[illegible]

Table 10 [illegible]
These compounds all showed a [illegible]ochromic [illegible] duction in intensity on change from [illegible]
All the monomers were found to obey Beer's [illegible]

The most surprising feature of [illegible] that all of the diolefins absorbed at [illegible] wavelength than the model compounds. [illegible] lected was cyclohexene. It [illegible] olefins were not shifting bathochromically [illegible] ly from this olefin. Since all of [illegible] tuted cyclohexenes, it was [illegible] 3-propylcyclohexene as a model [illegible] exhibited a bathochromic shift [illegible] in cyclohexene.

There must, therefore, be some unusual [illegible] operation to explain these strange results. If [illegible] had been interacting, a bathochromic shift would [illegible] predicted. The fact that 4-allylcyclohexene absorb[illegible] shorter wavelength than either cyclohexene or [illegible] hexene, clearly indicates that another factor is [illegible] tion.

It must be remembered that small effects [illegible] UV are undoubtedly due to many contributions. The [illegible] listed in Table 10, are actually the results o[illegible] ferent olefinic components [illegible]

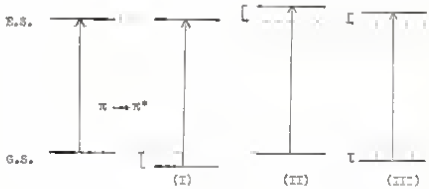
ULTRAVIOLET ABSORPTIONS OF SOME CYCLOHEXE[illegible]

Monomer	Absorption n-heptane (ε)	[illegible]
	179.1 (19,800)	[illegible]
	179.1 (21,500)	[illegible]
	180.5 (11,500)	[illegible]
	181.8 (18,800)	[illegible]
	18[illegible].8 (9,100)	[illegible]
	186.1 (9,700)	[illegible]

The observed λ_{max} is, in fact, the weighted average of the transition probabilities of the two types of double bonds, cis and vinyl. For example, the absorption of 3-allylcyclohexene (181.8 mμ) could arise from a mixture of allylcyclohexene (180.5 mμ) and 3-propylcyclohexene (186.1 mμ).

What will be attempted is an explanation of the hypsochromic shifts observed in 4-allylcyclohexene and 4-vinylcyclohexene. It does not seem possible to explain a hypsochromic shift by averaging the two longer wavelength absorptions. A tentative explanation will be offered which will have to suffice until a greater understanding of far ultraviolet spectroscopy is obtained.

To explain a hypsochromic shift, there can be but three general explanations. These possibilities are outlined below in terms of energy changes on the ground and/or excited states.



The first [illegible]
(G.S.) energy or to lo[illegible] it more [illegible]
(E.S.) energy is lowe[illegible]
the energy of the E.S. [illegible]
G.S. is raised. [illegible]
lowering the G.S. energy. [illegible]
possibilities is rather [illegible]
sented in the section o[illegible]
little or no ground [illegible]
this, hypsochromic e[illegible]
choice between (II) an[illegible]
resolve.

The only reasonable [illegible]
a combination of electron [illegible]
drawing (-I) inductive e[illegible]
of ionization potential (I.P[illegible]
that alkyl groups stabilize [illegible]
states. His calculations [illegible]
methyl is to stabilize the [illegible]
than the ground state. This [illegible]
with alkyl substitution.

A physical description [illegible]
by the removal of an electron [illegible]
This hole polarizes the [illegible]
charge is dispersed [illegible]

[illegible] more t[illegible] spectroscop[illegible] moved from the molecule[illegible] tal which is, however, [illegible] the π bond. Therefore, [illegible] considered to be left by [illegible]

Very little work [illegible] effects on ultraviolet [illegible] because it is extremely [illegible] and resonance effects. [illegible] Filler et al. (172) have [illegible] strongly electron [illegible] acids leads to hypsochromic [illegible]

Subst.	[illegible]
H	[illegible]
o-CF_3	[illegible]
m-CF_3	[illegible]
p-CF_3	[illegible]

Price et al. (17[illegible]) [illegible] CN groups all increase the [illegible] of arom[illegible] this as mainly a G.S. effect[illegible]

Although it is not [illegible] are mainly a G.S. or [illegible] thing similar to this [illegible]

hexene series. The relative effects of vinyl and allyl groups can be compared by their effects on pKa determinations. The relative -I effect of the vinyl is revealed by data by Brown (174).

	group	acid	pKa
	vinyl	COOH	4.25
decreasing -I	allyl	COOH	4.35
	propyl	COOH	4.82

The inductive effect of the vinyl is obvious from the comparison of 4-vinylcyclohexene (179.1 mμ) to cyclohexene (181.8 mμ). Here the vinyl has caused a hypsochromic shift, presumably through destabilization of the excited state. The fact that 3-allylcyclohexene absorbs at 181.8 mμ, the same as wavelength for cyclohexene, indicates that the +I effect of the allyl balances out the -I effect of the vinyl. The +I effect of the propyl is indicated by the bathochromic shift of 4.3 mμ from cyclohexene.

The lower value of 179.1 mμ for 4-allylcyclohexene relative to the 181.8 mμ value for 3-allylcyclohexene reflects the fact that the +I effect of the allyl has diminished with distance while the -I effect of the vinyl has not. This seems reasonable if one postulates a field effect for the induction caused by the vinyl group. Bartlett

and coworkers ([illegible]) [illegible]
rate retarding in [illegible]
by about 0.7 where [illegible]
indicates that [illegible]
manner rather than [illegible]

The compounds [illegible]
their extinction coefficients [illegible]
there is no evidence for inter[illegible]

The third group of monomers, [illegible]
behave in a similar manner. [illegible]
data for these monomers. Both [illegible]
hypsochromically with respect to [illegible]opentene. [illegible]

TABLE II

ULTRAVIOLET ABSORPTION OF [illegible]

Compound	n-Heptane λ_{max} (ε)	[illegible] λ_{max} (ε)
	3[illegible] ([illegible])	[illegible]
	182.[illegible] (1[illegible])	[illegible]
	18[illegible] (c,600)	[illegible]

again [illegible]
of the doubl[illegible]
allyl effect [illegible]
not so in the [illegible]
were about [illegible]
five-membered [illegible]
between the [illegible]
effect. Dried[illegible]
geometry allows th[illegible]ser a[illegible]

Finally, Table [illegible] con[illegible]
olefins. The diene appears [illegible]
by 1 mμ. Unfortunately, [illegible]
not available. Another C[illegible]
so that it would be too small [illegible]
since the accuracy of the [illegible] mμ.
Further work is necessary in [illegible]

TABLE 12

ULTRAVIOLET ABSORPTION OF SO[illegible]

Compound	n-Heptane λ_{max}	[illegible]	[illegible]	[illegible]
	179.0	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]

hexane c[illegible]. However, [illegible] monomer[illegible] ring closure experiments behaved [illegible] field effects of the second double [illegible] portant. The diolefins appeared [illegible] manner opposite to that which [illegible] is immediately apparent for [illegible] orientation effect of one double [illegible] important. That is, unless [illegible] in a[illegible] or [illegible] fashion, [illegible] stabilizing. Further [illegible] necessary.

Table 13 contains [illegible] monomers covering the region [illegible] monomer showed a small, but [illegible]

Olefins exhibit extre[illegible] (ϵ [illegible] in this region. The shelf [illegible] to 2[illegible] to 300 mμ depending on [illegible] absorptions were believed [illegible] triplet excitation of the [illegible] a forbidden transition since [illegible] not allowed. This single to [illegible] identified as occurring at [illegible] Evans (178). [illegible] again [illegible]

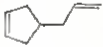
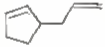
Monomer	n-Heptane λ_{max}	ϵ	λ	[illegible]
	222.5 259.0	(30.8) sh (2.0) sh	2[illegible]	[illegible]
	250.0 277.5	(4.0) sh (1.7) sh	[illegible]	[illegible]
	225.0 237.2 2[illegible]2.4 2[illegible]6.8 2[illegible]2.0	(18.8) sh (5.0) sh (.8) sh ([illegible]) sh ([illegible]) sh	[illegible] 2[illegible] 28[illegible]	[illegible]
	2[illegible]4.0 2[illegible].4 268.3 272.1 2[illegible].9	(7.6) sh (7.6) (1.0) (1.[illegible]) (1.5)	[illegible] [illegible] [illegible] [illegible]	[illegible]
	233.8	(7.5) sh	-	
	236.0 242.3 24[illegible] 2[illegible] 2[illegible]	(4.4) sh (6.9) ([illegible]) ([illegible])	-	

Table 13 (cont'd)

Monomer	n-Heptane λ_{max}	ϵ	95 EtOH λ_{max}	ϵ
	258.5	(2.7) sh	228.3	(14.4) sh
	266.3	(3.2)	263.4	(3.4) sh
	275.0	(2.2) sh		
	221.0	(9.5) sh	222.6	(3.5) sh
	258.6	(4.4) sh		
	261.0	(4.8) sh		
	264.3	(5.7)		
	267.3	(5.3)	267.3	(5.4) sh
	270.5	(6.9)	271.6	(5.8)
	274.0	(4.1) sh		
	277.3	(6.1)	278.4	(4.4) sh
	226.3	(70.9) sh	230.0	(77.9) sh
	242.8	(17.1)		
	248.5	(15.2)	248.5	(19.8) sh
	254.5	(14.8)	254.1	(16.0)
	258.0	(13.7)		
	260.9	(14.4)	260.5	(14.2)
	264.3	(14.6)	264.8	(13.6)
	267.8	(13.1)	268.3	(13.4)
	270.6	(15.4)	271.4	(13.3)
	273.6	(10.5) sh		
	277.3	(13.1)	279.8	(9.8) sh
	267.9	(3.7)		
	264.5	(3.6)		
	261.3	(4.4)		
	258.8	(4.4)		
	254.8	(4.3)		
	252.8	(4.5)		
	247.5	(5.2) sh		
	268.8	(0.3) sh	260	(0.2) sh

Table 13 (cont'd)

Monomer	n-Hex λ_{max}	ϵ	[illegible]	ϵ
	no max or shoulder max of 0.77 [illegible]		[illegible]	
	225.0 (3.9)-no shoulder		[illegible]	
	225.0 (0.3) no shoulder 238.8 (0.1) no			

transition unexplained as it is yet today. Berry (179) has attempted to explain it in terms of a $n-\pi^*$ analogy to formaldehyde.

Absorptions with such low values surely will be sensitive to impurities. Potts (180) has noted that oxygen affects these bands. Because of the uncertainty in the origin and the value of these absorptions, they will be reported but not discussed. One interesting feature is present. All the substituted cyclohexenes exhibit maxima in the region of 260-280 mμ while the cyclopentenes and cyclohexenes do not. This may prove of use for identification purposes if it is not due to an impurity or to oxygen.

The possibility that the transitions were from aromatic impurities was remote, since the diolefins were never in contact with any aromatic solvents or compounds. This resemblance must be superficial.

Other Physical Methods of Monomer Analysis

It has been proposed by Butler (139,140) that the non-conjugated interactions might be a ground state phenomena. It would seem logical then, to also investigate the monomers with a ground state instrument. Two such available methods were nuclear magnetic resonance (NMR) and infrared spectroscopy.

The allyl subst[illegible] opentenes a[illegible] all produced spectra [illegible] was ex[illegible] coupling and hence muc[illegible] the ab[illegible] Because of this sol[illegible] of τ [illegible] to specific protons wa[illegible] and [illegible] was decided that furthe[illegible] into [illegible] would have to be done [illegible] was not available.

The [illegible]MR spectr[illegible] discussed briefly dur[illegible] spectroscopy. A tempera[illegible] revealed any change in [illegible] room to [illegible] to -40°C. The room tem[illegible] spectrum of the [illegible] listed below with [illegible] methylenecyclo[illegible]

compound	C_2-(τ)	C_1, C_3 [illegible] τ
	5.57	7.[illegible]
	5.45	-
	5.18	-
	5.50	-

Conjugated terminal methylene groups generally absorb at 5.10 μ while unconjugated methylenes absorb at 5.35 μ (182). Since 1,4-dimethylenecyclohexane appeared to fall in the unconjugated region and the model exocyclic olefins behaved inconsistently, the investigation was not pursued further.

Infrared spectroscopy should be a suitable method for investigations of ground state interactions. A relationship exists between the force constant of the bond and its absorption frequency. This can be qualitatively shown by the following data:

bond type	force constant (10^{-5} $\frac{\text{dynes}}{\text{cm.}}$)	frequency range (cm.^{-1})
C-C	5	1100-1300
C=C	10	1500-1700
C≡C	15	2100-2300

Factors which affect the strength of the bonding would then be expected to also affect the infrared absorption frequency of that bond.

There is some evidence that the force constant is related to the mobile bond order (p) obtained from molecular orbital calculations. Work of Longuet-Higgins and Burkett on conjugated acetylenes supports this relationship (183).

If there is an interaction between non-conjugated diolefins, it might be possible to detect the interaction by

a decrease in the frequency of the carbon-carbon stretching frequency. As the carbon-carbon double bonds interact with each other, there should be more single bond character to the double bond, hence shifting the absorption to lower energies. In the usual example of ethylene, butadiene, the stretching frequency is shifted from 1623 cm.$^{-1}$ (Raman) in ethylene to 1597 cm.$^{-1}$ in butadiene.

Table 14 lists the stretching frequencies obtained on the monomers studied in this dissertation. There is clearly very little variance between the diolefins and the corresponding monoolefins. Such small differences as found in the table have no meaning since the accuracy of the infrared instrument used was just 4 cm.$^{-1}$.

It can be concluded that there is no evidence for interaction in these systems. Either the interaction is non-existent or too small to be detected with the above precision. It may also be that the above reasoning is not applicable.

Potts and Nyquist (184) have investigated the out-of-plane deformation frequency of the terminal methylene group. This absorption band is often referred to as a "methylene wag" since both hydrogen atoms move out of plane in the same direction. The authors found that this absorption is very sensitive to resonance effects of the substituents bonded to the olefin. A few typical examples are listed below.

TABLE 14

INFRARED ABSORPTION VALUES OF SOME UNSATURATED HYDROCARBONS

Compound	Formula	Frequency ($cm.^{-1}$)		
		NC=CH	$C=CH_2$	CH_2 wag
methylenecyclo-hexane		-	1651	887
dimethylene-cyclohexane		-	1655	890
methylenecyclo-cyclopentane		-	1660	872
3-allylcyclo hexene		1653	1642	912
4-allylcyclo-hexene		1651	1643	910
4-vinylcyclo-hexene		1652	1642	912
allylcyclo-hexane		-	1642	910
3-propylcyclo-hexene		1647	-	-

Table 14 (cont'd)

Compound	Formula	Frequency ($cm.^{-1}$)		
		HC=CH	$C=CH_2$	CH_2 wag
cyclohexene		1650	-	-
3-allylcyclo-pentene		1614	1642	910
4-allylcyclo-pentene		1616	1644	912
cyclopentene		1615	-	-
1,6-heptadiene		-	1642	910
1-hexene		-	1642	910

compound	wagging frequency ($cm.^{-1}$)
$OHC-CH=CH_2$	963
$NC-CH=CH_2$	960
$RCO-CH=CH_2$	955
$CH_3-CH=CH_2$	908
$\emptyset CH=CH_2$	906
$\emptyset OCH=CH_2$	851
$CH_3OCH=CH_2$	813

Substituents which donate electrons by resonance such as in methyl vinyl ether ($CH_3-\overset{\curvearrowright}{O}-CH=CH_2$) shift the absorption to lower frequencies. Electron withdrawing groups such as in acrylonitrile, shift the absorption in the opposite direction.

Table 14 also lists the experimental values for the wagging frequencies. Again, there is only a slight variation among the olefins. The abnormal value for the methylenecyclopentane probably reflects the greater strain caused by the smaller ring.

In summary then, there can be found no evidence for support of a ground state interaction in the systems studied.

Polymerization of the Monomers

The polymerization of 1,4-dimethylenecyclohexane was reported by Ball and Harwood in 1962 (185). Cationic

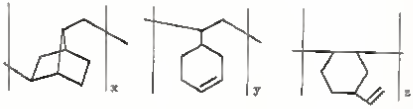
initiation of polymerization by boron trifluoride produced soluble polymers up to a 55 per cent conversion. Analysis of the polymer indicated it was composed of 96 per cent cyclic units (I). The intrinsic Zeigler polymerization of

(I)

the same monomer produced a 50 to 75 per cent soluble polymer with an intrinsic viscosity of 0.08. The polymer was obtained in 19 per cent yield of which 98 to 99 per cent was cyclic.

Butler and Miles (94) have polymerized 4-vinylcyclohexene into soluble, cyclic polymers. Boron trifluoride produced a 28 per cent yield of polymer assigned structure (II). The polymer was 85 per cent soluble and had an

(II)



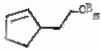
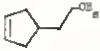
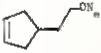
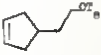
intrinsic viscosity of 0.11. Nuclear magnetic resonance (NMR) data indicated 65 per cent cyclization had occurred. Zeigler polymerization yielded in 20 per cent conversion, a

polymer which was 45 per cent soluble. The intrinsic viscosity was 0.04.

Brief reference was made in Chapter I to the solvolytic ring closure work of Closson (148), Bartlett (147) and Winstein (149). Table 15 lists an analysis of the product types from these and related solvolyses.

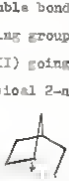
TABLE 15

PRODUCT TYPES FROM THE SOLVOLYSES OF SOME UNSATURATED ESTERS

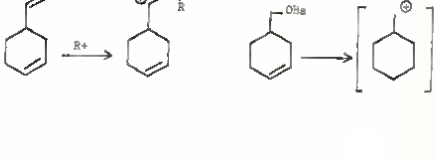
Compound[a]	% Cyclic	% Noncyclic	Reference
	0	100	Closson (148)
	97	3	Lawton (186)
	100	0	Lawton (186)
	92	8	Bartlett (147)
	80	20	Winstein (149)
	0	-	LeNy (187)

[a] Br=brosylate, Ms=mesylate and Ts=tosylate

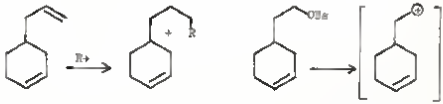
The solvolyses of the cyclopentenyl esters have been quite extensively studied. Closson concludes that solvolysis occurs through anchimeric assistance in the case of the 4-substituted-cyclopentenyl derivative but not in the case of the isomeric 3-substituted compound (148). Bartlett has established that there is a symmetric interaction of the double bond and in addition he has postulated maximum rate enhancements when the double bond is symmetrically oriented with respect to the leaving group (156). The intermediate may be represented by (III) going through the so-called "π-route" to the nonclassical 2-norbornyl bridged cation.

(III) 

Since such striking differences are found in the products by the symmetrical placement of the double bond, it was hoped that similar trends would be revealed during cationic polymerizations of the corresponding diolefins. It was encouraging to note that 4-vinylcyclohexene polymerized with about 65 per cent cyclization. Lefty had found that the corresponding solvolysis yielded no cyclic products. The structural analogies intended are represented below.



The fact that the polymer was only half cyclized allows an opportunity for increased cyclizations to be found in more suitable monomers. Such a monomer might be 4-allylcyclohexene. Winstein had found that the corresponding solvolysis yielded 80 per cent cyclic material. The relationship is depicted below.

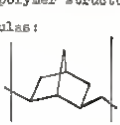


Predictions based on comparisons of the solvolytic data would then be that 4-allylcyclohexene should yield a much higher amount of cyclization than 4-vinylcyclohexene. Similar reasoning suggests that greater cyclization should occur in 4-allylcyclopentene than in 3-allylcyclopentene.

Cyclohexenes and cyclopentenes are known to polymerize cationically, but only slowly and in poor yields (188). Conversely, vinyl compounds can be polymerized much more readily by strong cationic catalysts (189). In the polymers to be studied, it is therefore assumed that initiation takes place on the allyl group. This assumption allows the analogy to be made between the intermediates in cationic polymerization and in the solvolyses.

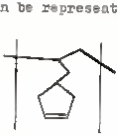
Tables referring to the polymerization conditions, product yields and per cent of soluble polymer appear throughout this section. Tables of data on the physical properties of the same polymers can be found in the appropriate part of the experimental section. Cationic polymerizations will be discussed first followed by discussion of the Zeigler polymers.

4-Allylcyclopentene was easily polymerized at -80°C. with boron trifluoride as shown in Table 16. An 84 per cent conversion to a polymer which was 96 per cent soluble was obtained. The intrinsic viscosity was 0.05 and the molecular weight indicated by vapor pressure determinations was 1786. This molecular weight corresponds on the average to approximately 15 monomer units per polymer chain. Infrared analysis revealed absorptions at 995 and 912 cm.$^{-1}$ (vinyl) and a very weak band at 675 cm.$^{-1}$ (cis double bond). The NMR spectra confirmed the presence of vinyls, 4.92τ and 5.19τ and of cis olefinic groupings, 4.34τ. The respective ratio of the two areas was 0.5 to 0.5 (sp^2 hydrogens) while the sp^3 hydrogen peak had a relative area of 42.6. The polymer structure can be represented by the following formulas:



90%

a = 12



3.3%

b = 10, c = 12

6.6%

d = 9, e = 3

TABLE 16

POLYMERIZATION OF 4-ALLYLCYCLOPENTENE

Polymer number	Monomer (moles)	Solvent (ml.)	Initiator System	[Ti]/[M][1] (moles)	[Al]/[Ti] (moles)	Reaction condition Temp. (°C)	Time	Polymer yield %	Polymer soluble %
IIa	7.5	n-heptane, 1.5	$TiCl_4$, $Al(Et)_3$	0.01	1	R.T.[2]	30 days	21	N.D.[3]
IIb	7.5	n-heptane, 1.5	$TiCl_4$, $Al(Et)_2$	0.01	2	R.T.	30 days	28	27
IIc	15.1	n-heptane, 6	$TiCl_4$, $Al(Et)_3$	0.01	2	50	35 days	32	70
IId	7.5	CH_2Cl_2, 10	BF_3(gas)			-80	28 hours	84	96
IIf	15.1	n-heptane, 6	$TiCl_4$, $Al(Et)_3$	0.01	2	R.T.	70 days	17	75

1 [M] = concentration of monomer in moles

2 R.T. - room temperature

3 N.D. = not determined

The percentage cyclization may be calculated from the NMR data by the following formula.

$$\% \text{ cyclization} = \frac{f-g\left[\frac{d}{e}\right]-\left[\frac{b}{c}\right]}{f+g\left[\frac{a-d}{e}\right]+\left[\frac{a-b}{c}\right]}(100)$$

where

a = number of sp^3 hydrogens in the saturated unit

b = number of sp^3 hydrogens in the uncyclized cis olefin containing unit

c = number of sp^2 hydrogens in the same unit

d = number of sp^3 hydrogens in the vinyl containing unit

e = number of sp^2 hydrogens in the vinyl containing unit

f = experimental ratio of sp^3/sp^2 (cis hydrogens)

g = experimental ratio of sp^2 (vinyl)/sp^2 (cis)

The experimental data must be corrected because one of the vinyl protons appears with the cis protons at 4.4 τ.

The formula can be applied to the NMR data given for poly(4-allylcyclopentene). Beneath the structures are listed the correct values of a, b, etc. Experimental values of f equal 42.6/0.33 and g equals 2/1 calculates to a percentage cyclization of 90 per cent.

The isomeric 3-allylcyclopentene (Table 17) polymerized to a fine white powder in 70 per cent yield. It was

TABLE 17

POLYMERIZATION OF 3-ALLYLCYCLOPENTENE

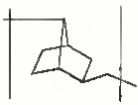
Polymer number	Monomer (mmoles)	Solvent (ml.)	Initiator System	Initiator [Ti]/[M] (mmoles)	Initiator [Al]/[Ti] (mmoles)	Reaction condition Temp. (°C)	Reaction condition Time	Polymer yield %	Polymer soluble %
IVa	15	n-heptane, 2.5	$TiCl_4$, $Al(Et)_3$	0.01	1	R.T.[5]	37 days	0.6	N.D.[2]
IVb	15	n-heptane, 2.6	$TiCl_4$, $Al(Et)_3$	0.01	2	R.T.	37 days	4	N.D.
IVc	15	n-heptane, 7.8	$TiCl_4$, $Al(Et)_3$	0.03	2	R.T.	40 days	2	N.D.
IVd	7.5	CH_2Cl_2,5	BF_3(gas)			-80[3]	24 hours	95	29
IVe	7.5	CH_2Cl_2,10	BF_3(gas)			-80	24 hours	70	73
IVf	15	n-heptane, 6	$TiCl_4$, $Al(i\text{-}Bu)_3$	0.10	2	50	8.5 days	7	75
IVg	10	n-heptane, 4.5	$TiCl_4$, $Al(Et)_3$	0.14	1	50	16 days	19	81
IVh	15	n-heptane, 6.0	$TiCl_4$, $Al(i\text{-}Bu)_3$	0.10	2	70	9 hours	9	53
IVi	15	n-heptane, 6.0	$TiCl_4$, $Al(i\text{-}Bu)_3$	0.10	2	70	21 hours	2.5[4]	N.D.

Table 1 (cont'd)

Polymer number	Monomer (moles)	Solvent (ml.)	Initiator System	[Ti]/[M][1] (moles)	[Al]/[Ti] (moles)	Reaction condition Temp. (°C)	Reaction condition Time	Polymer yield %	Polymer soluble %
IVj	15	n-heptane, 6.0	$TiCl_4$, $Al(i\text{-}Bu)_3$	0.10	2	70	56 hours	5.6[4]	67
IVk	15	n-heptane, 6.0	$TiCl_4$, $Al(Et)_3$	0.10	2	70	5.3 days	35	7
IVl	15	n-heptane, 6.0	$TiCl_4$, $Al(i\text{-}Bu)_3$	0.10	2	70	5 days	5	N.D.
IVm	15	n-heptane, 4.6	$TiCl_4$, $Al(Et)_3$	0.10	1	50	31 days	41	99
IVn	15	n-heptane, 6.8	$TiCl_4$, $Al(Et)_3$	0.15	1	50	21 days	39	92
IVo	15	n-heptane, 6	$TiCl_4$, $Al(Et)_3$	0.10	2	50	31 days	31	96
IVp	7.5	CH_2Cl_2, 15	BF_3(gas)			-80	24 hours	82	76

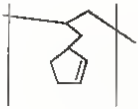
1 [M] = monomer concentration, moles
2 N.D.= not determined
3 allowed to warm to R.T. before termination of reaction
4 bath cooled to 40 per cent during polymerization, then reheated to 70°C.
5 R.T.= room temperature

found that 73 per cent was soluble and it had an intrinsic viscosity of 0.06. If the polymerization was allowed to warm to room temperature before termination with methanol, the yield of polymer increased to 95 per cent but only 29 per cent was then soluble. Infrared analyses revealed that all of the allylic groups had polymerized. This was confirmed by NMR which showed no measurable amount of sp^2 absorption. The experimental sp^3/sp^2 ratio could only be estimated as at least 111/1. Even extremely concentrated polymer solutions revealed no unsaturation. The structure of the polymer is represented below.



$> 95\%$

$a = 12$



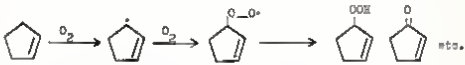
$< 5\%$

$b = 10,\ c = 2$

For a value of d > 111, the amount of cyclization is found to exceed 95 per cent. That some unsaturation still exists in the polymer was shown by the fact that the polymer was very prone to oxidation during handling. Infrared data indicated small amounts of absorption at about 1725 $cm.^{-1}$.

This is probably due to the grouping.

Allylic hydrogens are known to be susceptible to air oxidation by the following process (190):



Elemental analysis on polymer (IVa), handled routinely in the air, totaled only 94 per cent carbon and hydrogen. Subsequent analysis for oxygen revealed the missing 6 per cent was due to oxygen in the polymer. A second experiment was designed to determine if the oxygen was entering the polymer during isolation. All isolation and purification steps were performed in a dry box under a nitrogen atmosphere. All solvents which came in contact with the polymer were deaerated by the slow passage of nitrogen through the solvents. Analysis of this polymer showed that the oxygen content was decreased to only 2.5 per cent. The fact that oxygen was still present in the polymer was probably due to oxygen in the nitrogen supply and to the known inefficiency of the dry box. This reduction in oxygen content by almost 60 per cent indicates that atmospheric oxygen was the cause of the low analyses. It is somewhat surprising that the isomeric 4-allylcyclopentene did not exhibit this ease of oxidation.

3-Allylcyclohexene (Table 16) polymerized easily by boron trifluoride in 52 per cent conversion to a 91 per cent

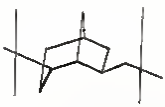
TABLE 18

POLYMERIZATION OF 3-ALLYLCYCLOHEXENE

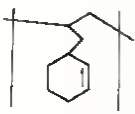
Polymer number	Monomer (moles)	Solvent (ml.)	Initiator System	[Ti]/[M][1] (moles)	[Al]/[Ti] (moles)	Reaction condition Temp. (°C)	Time	Polymer yield %	Polymer soluble %
IIIa	13.6	n-heptane, 2.4	$TiCl_4$ $Al(Et)_3$	0.01	1	R.T.[2]	37 days	10	N.D.[3]
IIIb	13.6	n-heptane, 2.5	$TiCl_4$ $Al(Et)_3$	0.01	2	R.T.	37 days	5	N.D.
IIIc	13.6	n-heptane, 8.3	$TiCl_4$ $Al(Et)_3$	0.04	2	R.T.	40 days	6	N.D.
IIId	6.8	CH_2Cl_2,5	BF_3(gas)			-80[4]	24 hours	88	94
IIIe	6.8	CH_2Cl_2,10	BF_3(gas)			-80	24 hours	52	91
IIIf	13.6	n-heptane, 3.1	TiCl Al(Et)	0.10	1	50	31 days	31	67
IIIg	13.6	n-heptane, 5.4	TiCl Al(Et)	0.10	2	50	21 days	19	71

1 [M] = concentration of monomer in moles
2 R.T. = room temperature
3 N.D. = not determined
4 after 5 hours allowed to warm to room temperature

soluble polymer. When the polymerization was allowed to warm to room temperature over 18 hours, both the polymer yield (88 per cent) and the solubility (94 per cent) increased. Both polymers proved to be highly cyclized (94 and 91 per cent, respectively) by infrared and NMR analysis. The polymers had intrinsic viscosities of about 0.05 and capillary melt temperatures of nearly 160°C. The structure of the polymer is represented below.



91-94%



9-6%

4-Allylcyclohexene (Table 19) was similarly polymerized by boron trifluoride in 64 per cent yield to a polymer which was 51 per cent soluble. Infrared analysis indicated the presence of unreacted vinyl groups (990 and 908 cm.$^{-1}$) and of cis double bonds (650 cm.$^{-1}$). This was confirmed by NMR with absorptions at 4.34, 4.93 and 5.13 τ. Based on the relative areas, the following structure can be represented for the polymer:

TABLE 19

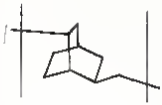
POLYMERIZATION OF 4-ALLYLCYCLOHEXENE

Polymer number	Monomer (moles)	Solvent (ml.)	Initiator System	[Ti]/[M][1] (moles)	[Al]/[Ti] (moles)	Reaction condition Temp. °C	Time	Polymer yield %	Polymer soluble %
Va	13.6	n-heptane, 4.1	$TiCl_4$, $Al(Et)_3$	0.01	1	50	7 days	87	68[2]
Vb	13.6	n-heptane, 5.4	$TiCl_4$, $Al(Et)_3$	0.01	2	50	7 days	52	98[2]
Vc	13.6	n-heptane, 5.4	$TiCl_4$, $Al(Et)_3$	0.01	2	R.T.[3]	7 days	51	N.D.
Vd	6.8	CH_2Cl_2, 15	BF_3(gas)			-80	24 hours	64	51

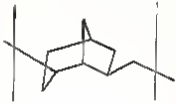
1 [M] = monomer concentration in moles

2 minimum figure based on isolated soluble polymer after one reprecipitation

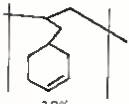
3 R.T. = room temperature



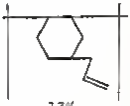
or



68%



19%



13%

Analysis of the data for the above monomer systems reveals no clear relationship between structure and the conversion or per cent soluble. There does appear to be a relationship between the monomers and per cent cyclization. Figure 3 reflects this trend. The monomers which were expected to yield exceedingly high amounts of cyclic product, are found to be no better than their 3-allylcycloalkene isosers. Based on the work of Miles and Butler (94), 4-vinylcyclohexene proves to be the poorest monomer for cyclization.

Instead of a symmetrical positioning of the double bond to the reaction site being the most important factor, it appears that the distance between the two may be significant. Figure 4 records the distances from the =CH— of the vinyl to the nearest carbon of the cis double bond. Calculations were made on Dreiding models and in the case

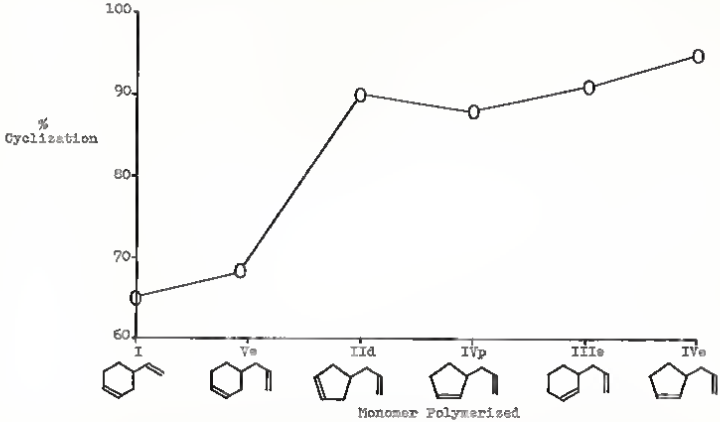


Fig. 3.--Relationship of per cent cyclization to the monomer polymerized.

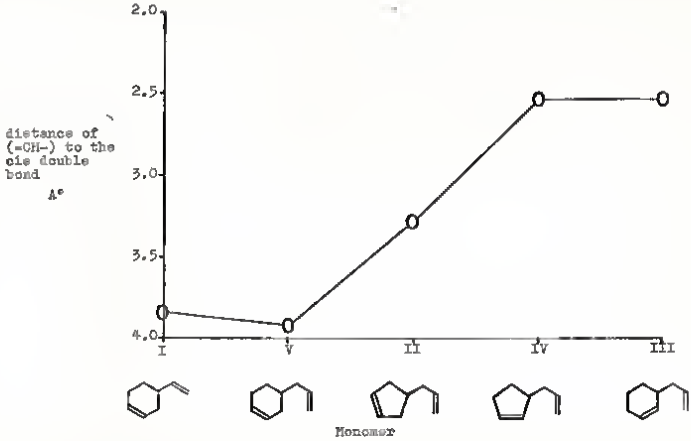


Fig. 4.-Separation of olefinic groupings in various monomers.

of the cyclohexenes the most stable ring conformations were selected. The rough paralleling of the two plots supports the supposition that distance is the major consideration. It must be taken into account that this interpretation is based on a small sample size. More determinations would be necessary to completely verify these results. For example, polymer IId appears slightly high. Further experiments might find this result is high and so it might be in better correlation with the other points.

Zeigler polymerizations have all been performed on these monomers. These polymerizations have been discussed as a separate group for the reasons listed below. The polymerization conditions can be found in the appropriate tables included earlier under the cationic discussion.

Although the exact mechanism of the Zeigler catalysis has not been established, certain features are quite well known. It is known that polymerization occurs at an active site on a heterogeneous catalyst. The monomer is thought to be preoriented on the catalyst surface before the actual polymerization. The coordination of the monomer to the polymerization site (thought to be the transition metal) occurs through the π electrons of the monomer. A recent examination of the Zeigler catalyst is available in a review edited by Raff and Dock (191).

Since the monomer is coordinated through its π electron system to a heterogeneous catalyst, it seems likely

that other factors besides interolefinic distances must be considered. One factor would be a knowledge of whether one or both double bonds are dependently or independently co-ordinated with the catalyst site. These considerations suggest that comparisons with solvolytic data might be extremely risky or even irrelevant. It is for these reasons that the Zeigler polymerizations are studied as a separate group and the major emphasis was placed on cationic polymerization.

The Zeigler catalyzed polymerization of all monomers except 4-allylcyclohexene proved to be exceedingly difficult. In all cases polymerization occurred but the predicament was in obtaining enough product for analysis. Since 3-allylcyclopentene was in relative abundance and appeared to be the most difficult to polymeriza, the majority of experimentations were done on this monomer.

Based on polymerizations of the 3-allylcycloalkenes, it was evident that at room temperature the conversion was too low and also too slow. To obtain satisfactory amounts of polymer it was necessary to run the reactions at elevated temperatures and with large amounts of catalyst. The increased conversion was obtained at the expense of the average molecular weight of the polymer. This was expected since it is known in other Zeigler polymerizations, the rate of the terminating steps increase faster than that of the propagating step with elevation of the temperature (191).

The structures proposed for the Zeigler polymers will be similar to those proposed during the cationic discussion. Reference should be made back to them at the appropriate time.

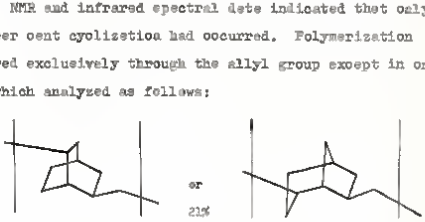
3-Allylcyclopentene (Table 17) polymerized optimally at 50°C. to 30 to 40 per cent yields of polymer which were greater than 90 per cent soluble. Table 16 summarizes the data for the many polymerizations. The preferred catalyst was triethylaluminum: titanium tetrachloride in a 2:1 ratio. The polymers were of very low molecular weight as indicated by intrinsic viscosities of 0.01 to 0.02. Vapor pressure molecular weights were about 1300. Infrared and NMR spectral data disclosed only residual cis unsaturation. The polymers were generally 70 to 80 per cent cyclized.

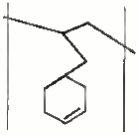
3-Allylcyclohexene (Table 18) was similarly polymerized at 50°C. to give very low molecular weight polymers. The polymers were very soluble in benzene and chloroform (97 and 98 per cent). An intrinsic viscosity of 0.01 and a molecular weight of about 1100 was obtained for one polymer. Infrared and NMR data revealed only cis double bond unsaturation. Calculations indicated the polymers to be about 70 per cent cyclic.

4-Allylcyclopentene (Table 16) polymerized at 50°C. to a very poor polymer. The polymer was not easily purified since it seemed to crosslink on handling. This monomer

gave a better polymer by polymerization at room temperature over a long period of time. A 17 per cent yield of 75 per cent soluble polymer was obtained after two months. Infrared and NMR evidence disclosed only 54 per cent cyclization.

4-Allylcyclohexene (Table 19) behaved quite strangely with Zeigler catalysis. Extremely high conversions in short periods of time were obtained either at 50°C. or at room temperature. Intrinsic viscosities of 0.1 to 0.45 indicated the polymers to be of quite high molecular weight. Per cent conversions of 51 to 87 per cent were obtained and they would probably have been increased if the polymerization media had not completely solidified. Difficulty in handling prevented an accurate determination of the per cent soluble. Indications were that the polymers were mostly soluble. The most carefully conducted isolation revealed a per cent of soluble polymer in excess of 98 per cent. NMR and infrared spectral data indicated that only 5-54 per cent cyclization had occurred. Polymerization occurred exclusively through the allyl group except in one case which analyzed as follows:





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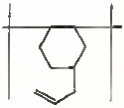
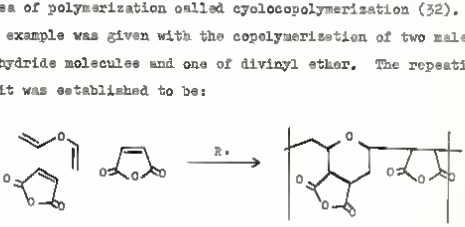


14%

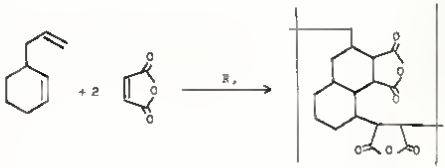
As was mentioned previously, the greater complexity of Zeigler catalysis makes predictions much less certain. This series of polymerizations revealed no definite trends as the cationic series did. The evidence suggested generally a greater cyclization and solubility with the 3-allylcycloalkenes, however. More experiments would be necessary to verify that such a trend is present.

Cyclocopolymerization of the Monomers

In Chapter I, a short discussion dealt with a new area of polymerization called cyclocopolymerization (32). An example was given with the copolymerization of two maleic anhydride molecules and one of divinyl ether. The repeating unit was established to be:

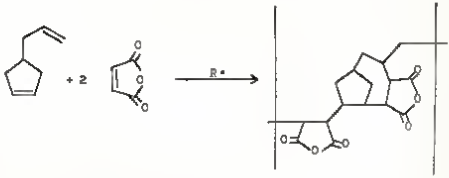


The 1,5-diolefins synthesized in this dissertation might also be able to undergo this type of copolymerization. An example would be maleic anhydride and 3-allylcyclopentene.



In the case of 1,5-diolefins, a six-membered ring could easily be formed by insertion of a maleic anhydride. The alternate seven-membered ring is possible but it is considered less likely so it will not be represented.

The 1,6-diolefins might also be able to cyclocopolymerize but in this case a seven-membered ring would have to be formed. This is represented below for the case of 4-allylcyclopentene.



The results of these copolymerizations are reported in Table 20. All the polymerizations were conducted in sealed vessels with azobisisobutyronitrile as the initiator. Solubility data were determined with dimethylformamide although dimethylsulfoxide was equally as good. The physical properties of the soluble copolymers are reported in Table 25, located in the experimental section.

The results of the polymerization can be more effectively shown by grouping the monomers by type. This can be shown as follows:

monomer	% soluble
1,5-dienes:	
4-vinylcyclohexene	100
3-allylcyclopentene	76
3-allylcyclohexene	94
1,4-dimethylenecyclohexane	0
1,6-dienes:	
4-allylcyclohexene	13
4-allylcyclopentene	0

The polymers appear to cleanly arrange themselves into two separate classes except for the case of 1,4-dimethylenecyclohexane. A closer analysis reveals that although the monomer is a 1,5-diene, the preferred site for radical attack will be the less hindered methylene end

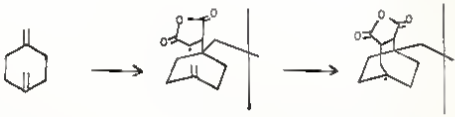
TABLE 20

POLYMERS OF SOME NON-CONJUGATED DIOLEFINS WITH MALEIC ANHYDRIDE

Comonomer	Polymer number	(moles) Monomer	Maleic anhydride	AIBN[1] (mm.)	Benzene (ml.)	Time	Temp. (°C.)	Polymer Yield %	Polymer Soluble %
4-vinylcyclohexene	Ig	10	11	20	10	6 hrs.	70	22	100
4-vinylcyclohexene	Ih	10	11	20	10	12 hrs.	70	36	100
4-vinylcyclohexene	Ii	10	11	20	10	36 hrs.	70	47	N.D.[2]
4-vinylcyclohexene	Ij	55	110	200	100	48 hrs.	70	31	100
4-vinylcyclohexene	Ik	55	121	200	100	10 days	50	43	100
4-allylcyclopentene	IIe	3.8	7.8	17.5	11	8 days	50	100	0
3-allylcyclohexene	IIIh	3.5	7.3	18.6	11	14 days	50	28	94
3-allylcyclopentene	IVq	3.7	7.9	13.2	11	8 days	50	56	76
4-allylcyclohexene	Vd	3.4	7.7	17.2	11	7 days	50	83	13
1,4-dimethylenecyclohexane	VIa	3.8	8.2	15.0	11	7 days	50	99	0

1 AIBN - α, α'-Azo-bis-isobutyronitrile
2 N.D. - not determined

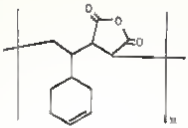
of the double bond. This means that the intermediate radical will probably react with the diolefins as if it had the following conformation.



The alternate possibility would put the radical on a primary carbon which is known to be an unfavorable situation (192).

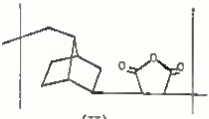
It seems reasonable then that 1,4-dimethylenecyclohexane should be classified under the 1,6-diolefin section since they all had to form seven-membered rings if they were to polymerize by this mechanism. Once this is done, the monomers group themselves nicely into two categories. The 1,5-diolefins each form highly soluble products while the 1,6-diolefins yield very low or insoluble polymers. The insoluble polymers probably represent a random polymerization with maleic anhydride to yield crosslinked gels.

The actual ratio of monomers in the repeating unit could be deduced from elemental analysis data. There are only three reasonable structures which may be considered as likely repeating units. The possibilities are shown below.



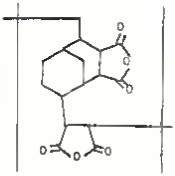
(I)

1:1 unsaturated copolymer



(II)

1:1 saturated copolymer



(III)

2:1 saturated copolymer

Both 4-vinylcyclohexene (94) and maleic anhydride (193) are known not to homopolymerize by free radical initiation. The fact that maleic anhydride prefers to alternate and that the diene does not polymerize free radically, makes (II) very

unlikely. Structures (I) and (III) were considered the most probable units.

Infrared analysis of the copolymer indicated a small amount of unsaturation. NMR indicated the presence of sp^2 hydrogens at 4.4 τ (cis olefin). The ratio of sp^2:sp^3 hydrogens was found to be about 1:23. Calculations for per cent cyclization based on repeating units of either (I) or (III) indicated 71 per cent cyclization had occurred.

Elemental analysis clearly indicated that the two to one copolymer had formed. The analytical possibilities are given below along with the data for the corresponding acids. The anhydride units are very susceptible to hydrolysis and consequently, it was extremely difficult to prevent some water uptake. The analysis for the completely hydrolyzed copolymer will be given to represent the limiting structure if it had all hydrolyzed. The expected results should fall between that of the anhydride and that of the acid, if the assignment is correct.

polymer type	theoretical analysis % C	% H
1:1 copolymer (anhydride)	69.88	6.84
1:1 copolymer (acid)	64.27	7.19
2:1 copolymer (anhydride)	63.15	5.30
2:1 copolymer (acid)	56.46	5.92
experimental result	62.36	5.70

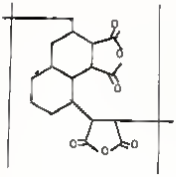
The analytical data indicated that the copolymer must be predominantly the 2:1 structure. Another sample of polymer was hydrolyzed completely and then analyzed. The data for this sample are listed below.

polymer type	theoretical analysis % C	% H
2:1 copolymer (anhydride)	63.15	5.30
2:1 copolymer (acid)	56.46	5.92
experimental anhydride	59.14	5.48
experimental acid	56.62	5.82

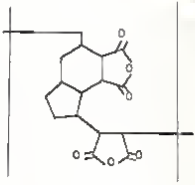
The data clearly indicates that the majority of the polymer is a 2:1 unit. Since some unsaturation did appear in the IR and NMR, it is presumed that there are some units of (I) in the polymer.

Elemental analyses also indicated 2:1 structures for the copolymers formed by 3-allylcyclohexene and 3-allylcyclopentene. 4-Allylcyclohexene gave small amount of soluble polymer which however, gave a very poor analysis. This polymer analyzed very low in carbon and hence must have included a large amount of maleic anhydride. The polymer proved also to be rather unstable. The polymer was not investigated further.

The soluble copolymers of 3-allylcyclohexene and 3-allylcyclopentene may be represented respectively as (IV) and (V) below.



(IV)



(V)

The polymers also revealed some unsaturation in their IR and NMR spectra. Therefore, there must also be some of the 1:1 unsaturated repeating units in these polymers. The NMR of these polymers were generally poor and not very eluci-dating. They will therefore, not be discussed.

There has recently appeared in the literature, a co-polymerization related to this work. Imoto (194) found that 4-(cyclohexen-3-yl)-pentene-1 (VI) copolymerized with maleic anhydride. The polymer was insoluble in sodium hydroxide. If this polymer were to proceed by the cyclic-

(VI)

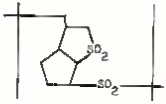
copolymerization mechanism, it would have to form eight- or nine-membered rings. Based on the foregoing results,

it is not surprising that only an insoluble polymer was obtained.

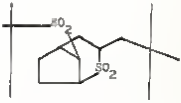
It remains to be seen whether other 1,5-diolefins will generally yield soluble copolymers. It is apparently critical that the second double bond be so oriented that it can open to yield a six-membered ring. Double bonds like those in 1,4-dimethylenecyclohexane would not be expected to satisfy this criteria. Apparently this reaction is only suitable for six-membered rings.

Another interesting area would be to copolymerize these and other similar 1,5- and 1,6-diolefins with carbon monoxide and sulfur dioxide. Polymers like the following should be possible.

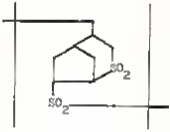
1,5-diolefin:



and/or



1,6-diolefin:



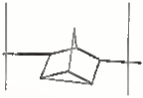
It would be interesting to see if soluble polymers were obtained.

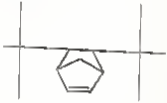
Correlation of the Data

The purpose of this section is to compare the experimental results in the ultraviolet and those in the polymerization portions of this dissertation. The objective is to determine if a relationship exists between the ultraviolet spectrum of a non-conjugated diolefin and its propensity to cyclopolymerize. Reference will be made to the research of others whenever it will contribute to the contents.

1,4-Dimethylenecyclohexane has been found to exhibit an unusual ultraviolet spectrum. This anomaly might be explained by an interaction between the transannularly located double bonds. Ball and Harwood had previously found that this compound could be polymerized into a polymer containing large percentages of cyclic units (155).

Norbornadiene is the only example of a system which definitely shows an interaction in the ultraviolet (129) and also cyclopolymerizes (195,196). Rabinowitz (195) has shown that free radical polymerization of this monomer yields a polymer containing up to 78 per cent norbornylene units. The polymer is represented below.





These two interacting systems have a common feature of limited flexibility. In 1,4-dimethylenecyclohexane the most reasonable conformations are shown below.

In a related compound, Orloski found interactions in the system with the ring locked in a boat conformation (132). The double bonds in norbornadiene are fixed because of the rigid ring structure.

The allylcycloalkenes synthesized in this dissertation were considered likely possibilities to show interactions. This was because the systems were somewhat restricted due to the alicyclic ring that was present. It was reasoned that the double bonds could never get as far apart as they are in a typical diene, such as 1,6-heptadiene, which shows no interaction. The high yields of cyclized products in the corresponding unsaturated tosylate solvolyses mentioned previously (Chapter I) also was a favorable indication.

The ultraviolet spectra of the allylcycloalkenes revealed no evidence for stabilization arising from an interaction between the two double bonds. The polymerization of these same monomers generally produced very high amounts of cyclization. On the basis of these experiments, there was definitely no correlation possible when both noninteracting and interacting monomers gave highly cyclized polymers.

Finding cyclic products even though no interaction was detected, suggests that the double bonds were not suitably aligned at the moment electronic excitation occurred. A ground state interaction, had it occurred, would have held the double bonds in such a position. The historical section on ultraviolet interactions clearly shows that suitably aligned chromophores can interact (Chapter I).

With the absence of an interaction, it must be concluded that no ground state interaction is occurring in these flexible systems. Support for this is provided by absence of any delocalization energy in norbornadiene (197). There is some doubt expressed by Dewar whether the resonance energy of butadiene is even as large as 2 kcal/mole (198).

Because the noninteracting monomers yielded cyclic polymers, the double bonds (or reactive intermediate) must have resided within the vicinity of one another at some point in time. Why was no evidence found for this?

Apparently, for flexible systems, there is no reason for the double bonds to be close together. When ultraviolet light is absorbed, it is so rapid that there is no possibility for the distant olefin to rotate into range through normal molecular rotation. The Franck-Condon principle forbids this (107, p. 134). For this reason ultraviolet spectroscopy does not seem to be a satisfactory method.

Therefore, unless there is some other compelling factor (rigid ring system for example) causing olefinic groups to be adjacent to one another, it should not be surprising that no identifiable interaction occurs. It must be concluded that no correlation will be possible in the typical non-conjugated diolefins studied.

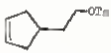
The fact that double bonds can interact with vacant p-orbitals in the transition state is well documented by solvolytic rate data where rate enhancements up to 10^{11} times faster than the saturated analogue can occur (199).

The principle driving force for cyclopolymerization must not reside in a π,π interaction but may result from the energy lowering caused by interaction of the double bond and a developing radical, anion or cation as the case may be. This resonance interaction lowers the energy of the cyclization step relative to that of the linear propagation. Other factors must be taken into account, however. Steric and

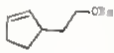
probability considerations may be more important in some cases.

For polymerizations which yield six-membered ring products, the energetics are apparently closely balanced between cyclic and linear propagation. In the polymerization of diallyl formal, cyclic polymerization is favored by 2.6 kcal/mole (14). The polymerization of acrylic anhydride (200,201) and methacrylic anhydride (202) indicates that the cyclic step is about 2.3 kcal/mole higher energy. Predominantly cyclic polymer is obtained since the pre-exponential term favors cyclization by a factor of 200.

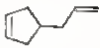
It is interesting to attempt an explanation why allyloycloalkenes were found to polymerize contrary to the expected results. Solvolysis data indicated a high percentage cyclization in (I) (147), but not in (II) (148). Polymerization of the corresponding diolefins, (III) and (IV), revealed that a greater amount of cyclization occurred in (IV) than (III).



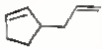
(I)



(II)



(III)



(IV)

An obvious explanation is that the two reactions are not exactly similar. The counter ion is known to effect some cationic polymerizations (203). Possibly this ion ($HOBF_3^{\ominus}$) is influencing the reaction.

CHAPTER III

EXPERIMENTAL

Equipment and Data

All temperatures are reported uncorrected and in degrees centigrade.

Ultraviolet (UV) spectra were obtained with a nitrogen purged Beckman Model DK-2A Ratio Recording Spectrophotometer equipped with far ultraviolet silica optics and cells. Wavelengths were calibrated with mercury emission lines.

Nuclear magnetic resonance (NMR) spectra were obtained either on a Varian V-4302 High Resolution Nuclear Magnetic Resonance Spectrometer or on a Varian A-60A Analytical NMR Spectrometer.

Infrared (IR) spectra were obtained either with a Perkin-Elmer Infracord Infrared Recording Spectrophotometer, a Perkin-Elmer Model 21 Infrared Recording Spectrophotometer or a Beckman IR IO Infrared Spectrophotometer.

Vapor phase chromatographic analyses (VPC) were carried out either on a F+M Model 700 Laboratory Chromatograph or on a Wilkens Aerograph Hi Fy Model 600-D Gas Chromatograph using helium as the effluent gas and a hydrogen flame detector.

Molecular weights were obtained on a Mechrolab Model 302 Vapor Pressure Osmometer with a 37°C. thermistor probe. All determinations were run in benzene solutions.

Refractive indices were obtained with a Bausch and Lomb Abbe 34 Refractometer equipped with an achromatic compensating prism.

Melting point determinations were performed in open capillary tubes in a Thomas-Hoover Melting Point Apparatus.

Intrinsic viscosities were calculated from efflux times of solutions through a Cannon-Ubbelohde Semimicro Dilution Viscometer set in a 25°C. constant temperature bath.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Sources and Purification of Materials

All common solvents and reagents were reagent grade products. The sources were Fisher Scientific Company, J. T. Baker Chemical Company, Matheson, Coleman and Bell and Eastman Organic Chemicals.

Boron trifluoride was obtained from The Matheson Company and used as received.

Triisobutylaluminum and triethylaluminum were obtained from the Ethyl Corporation and used as received.

Titanium tetrachloride was obtained from the Fisher Chemical Company and distilled before use.

Lithium aluminum hydride and sodium aluminum hydride were obtained from Metal Hydrides, Inc.

1,4-Cyclohexanedimethanol was obtained from Eastman Organic Chemicals and used as received.

Methylenecyclohexane, methylenecyclopentane and 1,6-heptadiene were obtained from the Columbia Organic Chemicals Company. 1-Hexene was obtained from Matheson, Coleman and Bell. 4-Vinylcyclohexene was obtained from KK Laboratories, Inc. Cyclohexene was obtained from Eastman Organic Chemicals. All olefins were distilled under N_2 from CaH_2 through a twenty-three plate spinning band column before use.

1,4-Cyclohexanediol was obtained from KK Laboratories and used as received.

The spectrograde solvents used in the spectra were supplied as follows: isooctane (Fisher Scientific Co.), heptane (Fisher Scientific Co.), acetonitrile (Eastman Organic Chemicals and Columbia Organic Chemical Co.), 95 per cent ethanol (Union Carbide).

Experimental Procedures for Ultraviolet Spectroscopy

Nitrogen purge.-A nitrogen purge of 1.5 ft^3/min. was used below 190 mμ and a purge of 0.3 ft^3/min. used between 190 and 210 mμ.

Concentration and pathlengths for solution spectra.-Below 210 mμ concentrations between 10^{-2} and 10^{-3} M were used with the 0.01 cm far UV cells. Above 210 mμ concentration of 10^{-1}M was used with 1 cm cells.

Absorbance[a] of Solvents Used in the Far Ultraviolet

wavelength (mμ)	n-heptane	iso-octane	aceto-nitrile	95% ethanol
200	.13	.08	.07	.11
197.5	.16	.08	.08	.13
195	.22	.09	.08	.16
192.5	.28	.09	.08	.15
190	.32	.10	.10	.40
187.5	.35	.10	.12	.78
185	.38	.10	.15	-
182.5	.38	.11	.24	-
180	.38	.19	.46	-
177.5	.37	.87	.90	-
175	.38	-	-	-
172.5	.48	-	-	-

[a]Solvent in sample cell vs nitrogen; 0.01 cm. Values are per cent absorbance.

Syntheses Related to Monomer Preparations

1,4-Cyclohexanedimethyl iodide.-This compound was prepared according to the procedure of Ball (151). A one liter, three-necked flask was equipped with a mechanical

stirrer, reflux condenser and a nitrogen inlet bubbler. The apparatus was charged with 72.0 g. (0.50 moles) of 1,4-cyclohexanedimethanol, 27.5 g. (0.876 moles) of red phosphorus and 350 ml. of reagent grade benzene. 195 g. (0.766 moles) of reagent grade iodine was added in reasonable amounts to the stirred slurry. The deep purple slurry was heated at reflux for forty-eight hours while copious amounts of HI was evolved. Gas evolution was practically nil after two days of refluxing. After cooling to room temperature, the yellow solution was decanted from the remaining tacky red solid. The solid was washed with two 200 ml. portions of benzene and the combined organic extracts were filtered through a glass frit. Benzene was removed under reduced pressure on a steam bath to yield a red liquid. The liquid was dissolved in a minimum amount of chloroform, methanol added and the solution cooled in an ice bath. Filtration yielded white crystals, first crop 73.5 g., m.p. 78-79°C. Further concentration yielded 59.9 g. and 8.2 g., m.p. 78-79°C. and 77-78.5°C., respectively. Total yield: 141.6 g. (79 per cent of theory). Recrystallization from ethanol yielded white crystals, m.p. 78-79°C.

1,4-Dimethylenecyclohexane.-This compound was also prepared according to the procedure of Ball (151). A 500 ml. three-necked flask was assembled with a mechanical stirrer, reflux condenser and a nitrogen inlet/bubbler. After the

apparatus was flamed out under nitrogen, 275 ml. [illegible] reagent-grade tert-butanol was added to the flask. To the stirred solvent, there was added in small increments, 14.88 g. (0.392 moles) of potassium metal. The solution was stirred at room temperature for 1.5 hours and then refluxed for an additional hour. The solution of potassium tert-butoxide was cooled slightly and 45.5 g. (0.125 moles) of recrystallized 1,4-cyclohexanedimethyl iodide was added in one portion. The solution was then refluxed for twenty-four hours, the white slurry cooled to room temperature and then treated carefully with 700 ml. of water. The organic layer was separated and washed four times (120 ml. total) with water. After drying over $MgSO_4$ the organic liquid was distilled through a spinning band column (twenty-three theoretical plates) to yield 6.03 g. (45 per cent of theory) of 1,4-dimethylenecyclohexane, b.p. 60-60.5°C. (98 mm.), $n_D^{19.5}$ 1.4734. VPC analysis over a dinonylphthalate column showed the presence of only one substance. Infrared analysis revealed the following absorption bands: 3080 and 2990 cm.$^{-1}$ (CH_2=), 1790 cm.$^{-1}$ (CH_2 out of plane overtone), 1655 cm.$^{-1}$ (C=C str.) and 890 cm.$^{-1}$ (CH out of plane). Ultraviolet absorption spectroscopy yielded the following data: iso-octane, 198.2 mμ (21,110), shoulder 202.8 mμ (18,514), shoulder 208.6 mμ (10,287); 95 per cent ethanol 198.6 mμ (19,454), shoulder 203.3 mμ (17,201), shoulder 208.9 mμ (9,554).

3-Chlorocyclopentene.-This compound was prepared according to the procedure of Noller and Adams (1958). A 300 ml., one-necked flask was charged with 73.7 g. (1.12 moles) of freshly cracked cyclopentadiene (b.p. 43°C.) and cooled to dry ice temperature. HCl gas was slowly bubbled into the diene until the gas was no longer absorbed (about two hours). The flask was then connected to a 1.5 x 12 cm. Vigreux distillation column and distilled under a water aspirator induced vacuum. Yield: 78.7 g. (69 per cent) of 3-chlorocyclopentene, b.p. 25-30°C. (26 mm.).

3-Allylcyclopentene.-Allylmagnesium chloride was prepared according to the procedure of Kharasch and Reinmuth (159). A one liter, three-necked flask was fitted with a mechanical stirrer, reflux condenser, addition funnel and nitrogen inlet/bubbler. The apparatus was flamed out twice under nitrogen, cooled to room temperature and charged with 26.7 g. (1.1 moles) of ether-washed magnesium metal and 400 ml. of anhydrous ethyl ether. The addition funnel was then loaded with 76.5 g. (1.0 moles) of redistilled allyl chloride in 75 ml. of anhydrous ether. The flask was cooled in an ice bath and the apparatus was placed under drying tubes. The allyl chloride solution was added slowly, over three hours, so that violent gas evolution did not occur. The white slurry was then stirred overnight at room temperature.

The addition funnel was recharged with 78.7 g. (0.7[illegible] moles) of 3-chlorocyclopentene in 100 ml. of anhydrous ether and then wrapped with a towel containing dry ice. The Grignard solution was cooled in an ice bath. The unsaturated halide was added slowly over two hours to the stirred Grignard solution and then the mixture was stirred at room temperature for twenty-four hours. The mixture was then carefully poured into a beaker of ice and acidified with a saturated solution of $(NH_4)_2SO_4$ until clear. The two phases were then filtered free of unreacted magnesium metal, the ether layer separated and the aqueous layer extracted four times (100 ml. each) with ether. The ether layers combined and dried over $MgSO_4$. Distillation through a 1.5 x 12 cm. Vigreux column yielded 38.1 g. (45.8 per cent) of colorless liquid, b.p. 81°C. (481 mm.) to 99°C. (386 mm.). $n_D^{20.5}$ 1.4514. Distillation through a spinning band column (twenty-three theoretical plates) yielded pure 3-allylcyclopentene, b.p. 95.5°C. (348 mm.), $n_D^{25.5}$ 1.4530, D_4^{20} 0.8039 g./ml. VPC analysis over a diisodecylphthalate column showed the presence of only one substance. NMR spectroscopy confirmed the assigned structure with absorptions at 4.36 τ (=CH), 5.10 τ ($=CH_2$) and 7.88 τ (CH,CH_2). Infrared analysis revealed the following absorption bands: 3095, 3070, 3015 and 2995 cm.$^{-1}$ (=CH and $=CH_2$), 1835 cm.$^{-1}$ (medium, $=CH_2$ out of plane overtone), 1650 and 1625 cm.$^{-1}$ (C=C), 995 and 915 cm.$^{-1}$

($-CH=CH_2$) and 720 $cm.^{-1}$ (cis,CH=CH). Other physical [illegible] ultraviolet spectroscopy, 182.3 mμ (17,367), n-heptane 182.7 mμ (15,416), acetonitrile. Near infrared spectrosc[illegible] 1,623 and 2.110 μ ($-CH=CH_2$) and 2.136 μ (cis CH=CH).

Anal. Calcd. for C_8H_{12}: C, 88.82, H, 11.18. Found: C, 89.05; H, 11.06.

4-Bromocyclopentene.-This compound was prepared according to the procedure of Bartlett and Rice (154). A 500 ml., three-necked flask was equipped with a mechanical stirrer, alcohol thermometer, pressure equalizing addition funnel and a Drierite drying tube. The apparatus was flamed out twice under a dry nitrogen atmosphere and then cooled to -40°C. by means of a dry ice/acetone bath. The flask was charged with 87.5 g. (1.33 moles) of freshly cracked cyclopentadiene (b.p. 43°C.) and 65 ml. of low boiling petroleum ether (dried by passage over neutral, activated alumina). The flask was maintained at -35 to -40°C. while 213.5 g. (1.33 moles) of bromine in 120 ml. of dry petroleum ether was slowly added from the addition funnel. Addition was complete within two hours to yield a white solid and a colorless supernatant liquid. The flask contents were transferred into a one liter Erlenmeyer flask and cooled -80°C. After cooling one-half hour, the supernatant liquid was decanted and the residual white solid was taken up in 450 ml. of anhydrous ethyl ether. Warming almost to room temperature was necessary for complete solution.

A one liter, three-necked flask was assembled with a mechanical stirrer, reflux condenser, pressure equalizing addition funnel and nitrogen inlet/bubbler. The equipment was flamed out twice under nitrogen and then cooled in an ice bath. The flask was charged with 22.0 g. (0.65 moles) of lithium aluminum hydride and 150 ml. of anhydrous ethyl ether. The ether solution of the above dibromide, was slowly added from the addition funnel over one hour. The gray slurry was stirred in an ice bath overnight behind two safety shields and then refluxed about forty-eight hours.

After cooling to room temperature, the gray slurry was filtered with suction through a large glass frit covered with a pad of glass wool. The tan filtrate was slowly poured into a large beaker of ice with rapid stirring. The ether layer was separated and the aqueous solution was extracted three times (150, 150, and 100 ml.) with ether, and distillation through a 1.5 x 12 cm. Vigreux column yielded 22.3 g. of colorless liquid, b.p. 77°C. (110 mm.) to 64°C. (37 mm.). Redistillation through the same column yielded 20.5 g. (10.5 per cent) of pure 4-bromocyclopentene, b.p. 53°C. (46 mm.) to 58.5°C. (47 mm.), n_D^{21} 1.5016. Infrared analysis revealed the following absorption bands: 3095 cm.$^{-1}$ (=CH), 1610 cm.$^{-1}$ (C=C, very weak) and 735 cm.$^{-1}$ (cis CH out of plane deformation).

The unsaturated bromide is stable only for a few days at room temperature, a week at 0°C., but it can be

stored for weeks, as a solid, at -80°C. with no noticeable decomposition.

4-Allylcyclopentene.-A 250 ml., three-necked flask was fitted with a mechanical stirrer, reflux condenser, pressure equalizing addition funnel and a nitrogen inlet/bubbler. The apparatus was flamed out twice under nitrogen, cooled and then charged with 5.57 g. (0.229 moles) of ether-washed magnesium metal, 60 ml. of anhydrous ether and a crystal of iodine. The addition funnel was loaded with 33.57 g. (0.229 moles) of 4-bromocyclopentene in 50 ml. of anhydrous ether. A small amount of the halide was added to the magnesium metal and then stirred until the reaction commenced. The additional halide was added over two hours at a rate to maintain a gentle reflux. The reaction was then refluxed two hours and cooled to room temperature.

A 500 ml., three-necked flask was fitted with a mechanical stirrer, reflux condenser, pressure equalizing addition funnel and $CaSO_4$ drying tubes after having been flamed out twice under nitrogen. The mechanical stirrer of the flask containing the Grignard reagent was replaced by a tube containing a glass wool plug. The Grignard solution was forced through the plug into the 500 ml. flask by means of nitrogen pressure. The unreacted magnesium was washed twice with 20 ml. portions of anhydrous ether. The Grignard solution was cooled in an ice bath while the addition funnel

was charged with 27.3 g. (0.229 moles) of freshly [illegible] allyl bromide in 200 ml. of anhydrous ether. The allyl bromide solution was added slowly to the Grignard solution over two hours with stirring. The solution was allowed to warm to room temperature while stirring overnight. The reaction product was a light yellow solution with a large amount of red-brown oil at the bottom of the flask. The mixture was poured slowly onto a beaker of ice and treated with a saturated solution of $(NH_4)_2SO_4$ until clear. The ether layer was separated and the aqueous layer extracted three times (200, 100, 100 ml.) with ether. The combined ether fractions were dried over $MgSO_4$ and then distilled through a 1.5 x 12 cm. Vigreux column. Yield: 12.9 g. of colorless liquid, b.p. 105-123°C. The distillate was carefully fractionated through a spinning band column (twenty-three theoretical plates) to yield 10.1 g. (40.9 per cent) of 4-allylcyclopentene, b.p. 121-122°C. (760 mm.), n_D^{21} 1.4511, d_4^{20} 0.8141 g./ml. Infrared analysis revealed the following absorption bands: 3090, 3070, 3010 and 2985 cm.$^{-1}$ (=CH and =CH_2), 1835 cm.$^{-1}$ (weak, =CH_2 out of plane overtone), 1650 and 1620 cm.$^{-1}$ (C=C, strong and medium), 992 and 912 cm.$^{-1}$ (-CH=CH_2), and 670 cm.$^{-1}$ (cis C=C out of plane deformation). Nuclear magnetic resonance (NMR) spectroscopy confirmed the structure. Vapor phase chromatography over diisodecylphthalate and β,β'-oxydipropionitrile columns

showed only one substance to be present. Other physical data: Ultraviolet spectroscopy, 180.0 mμ (18,521), n-heptane 180.6 mμ (19,340), acetonitrile. Near infrared spectroscopy, 1.632 and 2.115 μ ($-CH=CH_2$) and 2.137 μ (cis CH=CH).

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.95; H, 11.36.

3-Bromocyclohexene.-This compound was prepared according to the procedure of Bailey and Nicholas (160). A two liter, three-necked flask was equipped with a mechanical stirrer, reflux condenser and a nitrogen inlet/bubbler. The apparatus was then charged with 38.9 g. (0.476 moles) of freshly distilled cyclohexene (b.p. 83.0-83.5°C), 76.9 g. (0.437 moles) of recrystallized N-bromosuccinimide, 0.17 g. of benzoyl peroxide and 650 ml. of carbon tetrachloride. The mixture was refluxed for two hours, cooled to room temperature and insoluble succinimide (41.5 g., 96% of theory) was filtered off and washed twice with fresh solvent. Carbon tetrachloride was distilled off at atmospheric pressure through a 1.5 x 15 cm. glass helices packed column. 3-Bromocyclohexene was then collected by distillation at reduced pressure through a 1.5 x 12 cm. Vigreux column. The first distillation yielded 39.53 g. (56.2 per cent of theory) of colorless liquid, b.p. 55-58°C. (12 mm.). Redistillation through the same column yielded pure 3-bromocyclohexene, b.p. 60-62°C. (15 mm.), n_D^{20} 1.5308. Infrared analysis

yielded the following absorption bands: 30[illegible] [illegible]$^{-1}$ [illegible] 1645 cm.$^{-1}$ (C=C) and 730 cm.$^{-1}$ (cis CH=CH).

3-Allylcyclohexene.-Allylmagnesium chloride was prepared according to the procedure used in the preparation of 3-allylcyclopentene. A one liter, three-necked flask was charged with 6.80 g. (0.280 moles) of magnesium metal and 100 ml. of anhydrous ether. 21.0 g. (0.275 moles) of freshly distilled allyl chloride dissolved in 100 ml. of anhydrous ether was caused to react with the magnesium and then stirred at room temperature overnight.

The addition funnel was loaded with 37.5 g. (0.233 moles) of 3-bromocyclohexene in 200 ml. of anhydrous ether. The unsaturated bromide was added at a rate to maintain a gentle reflux. Time of addition was seventy minutes. The reaction mixture was then stirred overnight at room temperature. The resulting white slurry was poured slowly into a beaker of ice and acidified with a saturated solution of $(NH_4)_2SO_4$ until clear. The ether layer was separated and the aqueous layer extracted three times (100,50,50 ml.) with ether. The combined ether extracts were dried over $MgSO_4$ and then distilled through a 1.5 x 12 cm. Vigreux distillation column. Yield: 17.91 g. (71.5 per cent of theory) of colorless liquid, b.p. 92.5°C. (101 mm.) to 85°C. (70 mm.). Distillation through a spinning band column (twenty-three theoretical plates) yielded pure 3-allylcyclohexene, b.p.

88°C. (89 mm.), n_D^{20} 1.4682, d_4^{20} 0.8264 g./ml. [illegible] over a diisodecylphthalate column showed the presence of only one compound. NMR spectroscopy confirmed the [illegible] structure with absorptions at 4.44 τ (=CH), 5.08 τ [illegible] and 8.15 τ (CH,CH_2). Infrared analysis revealed the following absorption bands: 3090, 3080, 3030 and 2995 cm.$^{-1}$ (=CH and =CH_2), 1835 cm.$^{-1}$ (weak, =CH_2 out of plane overtone), 1650 and 1660 cm.$^{-1}$ (C=C), 995 and 915 cm.$^{-1}$ [illegible] and 725 and 685 cm.$^{-1}$ (cis, CH=CH). Other physical data: ultraviolet spectroscopy, 181.8 mμ (18,841), n-heptane; 183.0 mμ (17,614), acetonitrile. Near infrared spectroscopy, 1.620 and 2.110 μ (-CH=CH_2) and 2.135 μ (cis CH=CH).

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.49; H, 11.46.

4-Chlorocyclohexanol.-This compound was prepared according to the procedure of Owens and Robins (161). 100 g. (0.86 moles) of cis, trans-1,4-cyclohexanediol and 200 ml. of concentrated HCl was split into three equal portions. Each fraction was placed in a 400 ml. hydrogenation bottle and shaken at 80-90°C. for approximately twenty-two hours. The three portions were combined, the dark brown organic layer separated and the aqueous acid layer extracted three times (150 ml. total) with fresh chloroform. The combined chloroform washings were treated twice with water (75 ml. total), washed once with 40 ml. of 5 per cent $NaHCO_3$ and

dried over $MgSO_4$. Di[illegible] through a 1.[illegible] x [illegible] cm Vigreux column yielded 72.[illegible] g. (52 per cent of [illegible]eory) of crude 4-chlorocyclohexanol, b.p. 70°C. (5 mm.) to 78°C. (3 mm.), n_D^{19} 1.4937. VPC analysis over a carbowax 20M column revealed the presence of about eight substances. Infrared analysis revealed the following absorption bands: 3400 cm.$^{-1}$ (-OH), 1065 cm.$^{-1}$ (OH) and 745 cm.$^{-1}$ (C-Cl).

4-Chlorocyclohexene.-This compound was prepared according to the procedure of Birch and Hunter (162). A 200 ml., three-necked flask was fitted with a nitrogen inlet and a 1.5 x 12 cm. Vigreux column-distilling head combination. This was set up for downward distillation. The flask was charged with 72.2 g. (0.537 moles) of redistilled 4-chlorocyclohexanol and 3.3 g. of β-naphthalenesulfonic acid. The mixture was heated by means of an oil bath maintained at 220-230°C. A distillate of water first appeared and then the unsaturated halide distilled over a maximum temperature of 156.5°C. The reaction time was one hour. The resulting two-phase system was treated with methylene chloride (50 ml.). The organic layer separated and the remaining aqueous layer extracted three times (20, 20, 20 ml.) with methylene chloride. After drying over $MgSO_4$, the crude unsaturated halide was obtained by distilling through a 1.5 x 12 cm Vigreux column. The reaction yielded 41.93 g. (67 per cent) of colorless li[illegible]uid, b.p. 77°C. (110 mm.)-72°C.

(55 mm.). This material [illegible] the same column to yield 40.92 g. of pure 4-chlorocyclohexene, b.p. 81.5-82°C. (115 mm.), n_D^{20} 1.4325. VPC analysis over a Carbowax 20M column showed the compound to be 99 per cent pure. Extremely small amounts of three lower boiling substances were visible. Infrared analysis revealed the following absorption bands: 3095 cm.$^{-1}$ (=CH), 1650 cm.$^{-1}$ (C=C) and 675 cm.$^{-1}$ (cis, CH=CH).

<u>4-Allylcyclohexene</u>.-A 500 ml., three-necked flask was equipped with a mechanical stirrer, pressure equalizing addition funnel, reflux condenser and a nitrogen inlet/bubbler. The apparatus was flamed out twice under nitrogen, cooled to room temperature and then loaded with 8.8 g. (0.36 moles) of ether-washed magnesium metal, a crystal of iodine and 100 ml. of anhydrous ethyl ether. Into the addition funnel was placed 38.5 g. (0.33 moles) of redistilled 4-chlorocyclohexene in 100 ml. of anhydrous ether. A small amount of the halide was added to the magnesium metal and then the mixture was vigorously refluxed for forty minutes before the reaction began. The remaining halide was added over 1.5 hours while the reaction was cooled in ice.

A one liter, three-necked flask was equipped with a mechanical stirrer, pressure equalizing addition funnel, reflux condenser and drying tubes after flaming out the

apparatus under nitrogen. The Grignard solution was filtered into the one liter flask exactly as described in the preparation of 4-allylcyclopentene. To the ice cooled Grignard solution was added 40.3 g. (0.331 moles) of freshly distilled allyl bromide (b.p. 70°C.) in 200 ml. of anhydrous ether. The time of addition was 1.5 hours. An additional 100 ml. of ether was added to the yellow-green solution since the precipitated white salts were too thick to allow easy stirring. The slurry was stirred overnight at room temperature, refluxed one hour and then poured into a beaker of ice after cooling. Saturated $(NH_4)_2SO_4$ was used to clarify the solution. The ether layer was separated and the remaining aqueous layer was extracted three times (200, 100, 100 ml.) with ether and dried over $MgSO_4$. Distillation through a 1.5 x 12 cm. Vigreux column yielded 24.21 g. (59.9 per cent) of colorless liquid, b.p. 89-95 (130 mm.). This material was carefully fractionated through a twenty-three plate spinning band column to yield pure 4-allylcyclohexene, b.p. 97°C. (132 mm.), $n_D^{20.5}$ 1.4658, $d_4^{20.5}$ 0.8320. NMR supported the structure with absorptions at 4.42 τ (CH=), 4.95 and 5.18 τ (CH_2=), and 8.03, 8.34 and 8.50 τ (CH,CH_2). VPC analysis over a diisodecylphthalate column showed the presence of only one material. Infrared analysis revealed the following absorption bands: 3080, 3385 and 2085 cm.$^{-1}$ (CH= and CH_2=), 1830 cm.$^{-1}$ (CH_2=CH out of plane overtone),

1655 and 1645 cm.$^{-1}$ (C=C stretch), 990 and 9[illegible] out of plane, vinyl) and 650 cm.$^{-1}$ (CH out of [illegible]). Near infrared analysis revealed vinyl absorptio[illegible] and 2.117 μ and cis CH=CH absorption at 2.138 μ. [illegible] violet analysis revealed the following absorptions: [illegible] mμ (21,545), n-heptane: 179.8 mμ (19,471) acetonitrile.

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.32; H, 11.61.

Allylcyclohexane.-This compound was prepared using the general procedure of Rassequier (1963) with this author's modifications. A 500 ml., three-necked flask was fitted with a mechanical stirrer, addition funnel, reflux condenser and mercury bubbler. The Grignard reaction was conducted in the usual manner on 81.5 g. (0.5 moles) of freshly distilled cyclohexyl bromide (b.p. 95°C./97 mm.) [illegible] 100 ml. of dry ether and 13.3 g. (0.56 moles) of magnesium metal covered with 75 ml. of ether. The reaction was started with iodine and then cooled in ice while the remainder of the alkyl bromide was added. Time of reaction was two hours.

A one liter, three-necked flask equipped in the usual way was charged with the filtered Grignard solution. The addition funnel was loaded with 60.5 g. (0.5 moles) of freshly distilled allyl bromide (b.p. 70°C.) [illegible] 100 ml. of ether. The allylic halide was added over two hours to the ice-cooled Grignard solution. After stirring at room

temperature for 24 hours, the [illegible] at a colorless upper layer and a light brown oil. [illegible] poured onto ice, acidified with NH_4Cl and extrac[illegible] repeatedly with ether. After drying, the product [illegible] obtained by distillation through a 1.5 x 15 cm. Vigreux column. The olefin was collected in two fractions, 57.0 g. (92 per cent), the majority boiling at 99°C. (155 mm.). Distillation through a 23 plate spinning band column yielded pure allylcyclohexane, b.p. 94°C. (129 mm.), n_D^{20} 1.4505. NMR supported the structure with absorptions centering at 4.25, 5.10 and 8.5 τ. The ratio of sp^2 to sp^3 hydrogens experimentally found (1:12.98) was in excellent agreement with theory (1:13). VPC analysis over a diisodecylphthalate column revealed the presence of only one material. Infrared analysis revealed the following absorption bands: 3084 and 2981 cm.$^{-1}$ (=CH_2, =CH stretch), 1842 cm.$^{-1}$ (overtone of out of plane deformation), 1642 cm.$^{-1}$ (C=C), 995 and 910 cm.$^{-1}$ (vinyl out of plane deformation). Ultraviolet analysis revealed the following absorptions: 180.5 mμ (11,500), n-heptane; 181.1 mμ (10,500), acetonit[illegible]le.

Anal. Calcd. for C_9H_{16}: C, 87.02, H, 12.98. Found: C, 87.08; H, 12.99.

3-Propylcyclohexene.-This compound was prepared according to the procedure of Berlande (164). n-Propylmagnesium bromide was prepared similarly to the synthesis o[illegible]

4-bromocyclopentene. A 500 ml., three-necked f[illegible] fitted with the usual equipment. 52.8 g. (0.42[illegible] moles, 10 per cent mole excess) of redistilled propyl bromide (b.p. 69-71°C.) in 150 ml. of ethyl ether was reacted with 9.9[illegible] g. (0.429 moles) of ether-washed magnesium metal and 50 ml. of ether. The alkyl bromide was added over two hours and the mixture was stirred at room temperature for 1.5 hours.

A one liter, three-necked flask w[illegible] fitted with mechanical stirrer, reflux condenser, addition funnel and $CaSO_4$ drying tubes after having been flamed out twice under nitrogen. The flask was charged with the filtered n-propylmagnesium bromide solution above. 62.85 g. (0.39 moles) of freshly distilled 3-bromocyclohexene in 130 ml. of dry ether was added slowly to the cooled ice/salt Grignard solution. Time of addition was two hours. The reaction mixture was allowed to warm to room temperature overnight (18 hours). The light yellow solution and brown oil was poured into ice and clarified with a saturated NH_4Cl solution. The ether layer was separated and the aqueous layer was extracted five times (500 ml. total), combined and dried over $MgSO_4$. Distillation through a 1.5 x 15 cm glass helices column at atmospheric pressure yielded 27.4 g. (56.6 per cent) of crude 3-propylcyclohexane, $n_D^{20.5}$ 1.4599, b.p. 148°C.-151°C. Distillation through a 23

plate spinning band column [illegible] yielded the coorest fraction, b.p. 157.5-158°C. VPC analysis of a 9 foot SE-30 silicon column revealed the presence of 2 per cent of impurity. This impurity was probably 3-bromocyclohexene as shown by a rapid precipitate with alcoholic silver nitrite solution.

The impurity was removed by stirring and shaking with excess aqueous silver nitrate solution. The olefin was taken up in pentane, dried and passed over a small column of activity grade one alumina. 3-Propyl was distilled in a 23 plate spinning band column. Yield: a small amount of pure product n_D^{20} 1.4580. Infrared analysis revealed the following absorption bands: 3020 cm.$^{-1}$ (=CH stretch), 1647 cm.$^{-1}$ (C=C stretch), 710 and 665 cm.$^{-1}$ (cis, CH=CH out of plane deformation) and 735 cm.$^{-1}$ (propyl). NMR spectra supported the structure with an absorption centered at 4.35 τ and a quartet centered at 8.93 τ and a triplet centered at 9.34 τ. The ratio of sp^2 to sp^3 hydrogens experimentally found (1:7.09) was in good agreement with theory (1:7). Ultraviolet analysis revealed the following absorptions: 186.1 mμ (9,300), n-heptane, 186.4 mμ (8700), acetonitrile.

<u>Anal.</u> Calcd. for C_9H_{16}. C, 87.02; H, 12.98. Found: C, 86.88; H, 13.05.

Polymerizations

The intrinsic viscosities of all polymers were determined at 25°C. in benzene and of the copolymers in dimethylformamide. The method of calculation can be found in any textbook of polymer chemistry.

Infrared data was obtained on all polymers using potassium bromide pellets. Nuclear magnetic resonance data were obtained on the polymers in chloroform-d_1 and on the copolymers in D_2O or dimethylsulfoxide-d_6.

Capillary melt temperatures were recorded on the polymer at the moment visible shrinkage began to occur in the solid powder. This was found to approximate the polymer melt temperature and was much simpler.

The experimental techniques for the polymerizations conducted in this study may be adequately represented by a single example in each area. The three areas of polymerization were cationic, Zeiglar and free radical copolymerizations.

The physical properties of the polymers and copolymers prepared in this study are given in Tables 21, 22, 23, 24, and 25. This data can be referred back to the polymerization conditions listed in Chapter II, by the use of the number assigned to each polymer.

Poly-(4-allylo[illegible]). [illegible] flask was equipped with a mechanical stirrer, [illegible] inlet and a reflux condenser-mercury bubbler combination. The apparatus was flamed out once under nitrogen and then cooled in an isopropanol-dry ice bath. Ten ml. of reagent methylene chloride was added to the flask while a slow nitrogen stream was maintained. After ten minutes, 1 ml. (0.81 g., 7.9 moles) of 4-allylcyclopentene was added by means of a hypodermic syringe. Following five additional minutes of cooling, the nitrogen flow was replaced by a gentle stream of BF_3 gas. The colorless solution turned orange-brown almost immediately. The BF_3 gas flow was terminated after nine minutes and the equipment was sealed with glass stoppers. The flask was stirred for four hours, sealed and stored in a large Dewar flask containing isopropanol-dry ice for twenty-four hours. At this time the flask contained orange-brown liquid (viscous) and traces of solid. The polymer was isolated by introduction into the flask of 50 ml. of reagent methanol already cooled to -70°C. The polymer immediately precipitated as a fine white poly[illegible]. The polymer slurry was transferred into a beaker with methanol until the total volume reached 350 ml. Then the slurry was stirred magnetically for one hour, allowed to stand overnight, filtered off, and dried twenty-four hours under vacuum at 50°C. to yield 0.58 g. (84 per cent) of white

polymer. The polymer was treated with [illegible] form, filtered free of insoluble material [illegible] cent) and reprecipitated by dropwise addition [illegible] stirred methanol. Filtration, washing and [illegible] 0.61 g. of white solid. Following a second reprecipitation the following data were obtained: capillary melt temperature 157°C., intrinsic viscosity of 0.05 in benzene, molecular weight 1786. The infrared data revealed the following absorption bands: 2940 and 2870 cm.$^{-1}$ (C-H), 1650 cm.$^{-1}$ (C=C), 1460 cm.$^{-1}$ (CH_2), 990 and 905 cm.$^{-1}$ ($CH=CH_2$). The NMR determined ratio of sp^3 to sp^2 hydrogens was 42.6:1.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found C, 88.92; H, 11.10.

Poly-(3-allyloyclohexene).--All of the following equipment was flushed overnight in a dry box by a rapid nitrogen flow. All loading operations were conducted in the same inert atmosphere. A specially constructed polymerization bottle consisting of a 24/40 ₮ top and a 50 ml., 24/40 ₮ bottom was charged with 2.7 ml. (1.35 mmoles) of a 0.5 M-$TiCl_4$ solution in n-heptane and 2.7 ml. (2.70 mmoles) of a 1.0 M-triethylaluminum solution in n-heptane. The dark brown precipitate was aged only a few minutes and then 2.0 ml. (1.65 g., 13.6 mmoles) of 3-allyloyclohexene (freshly distilled from CaH_2) was added to the slurry. The bottle was then wired shut and placed in a constant temperature bath

at 50°C. The bottle was [illegible] each day until isolation, twenty-one days [illegible]. [illegible]ation of the polymer was achieved by pouring [illegible] the bottle slowly into 300 ml. of magnetically [illegible] methanol. The bottle was washed out with an additional [illegible] solvent. After stirring for one hour, the [illegible] cloudy solution was allowed to stand o[illegible]. The resulting clear, light brown solution was [illegible] bath briefly, cooled to room temperature and [illegible] to yield 0.32 g. (19.4 per cent) of white polymer. [illegible] was taken up in 20 ml. of chloroform, filtered [illegible] soluble material (0.01 g., 3 per cent) and twice [illegible]tated by dropwise addition to stirred methanol. [illegible] 0.25 g. of white polymer with the following properties: capillary melt temperature of 80°C., intrinsic [illegible] 0.01 in benzene, molecular weight 1924. The infrared [illegible] revealed the following absorption bands: 3050 cm.$^{-1}$ ([illegible]), 2930 and 2860 cm.$^{-1}$ (C-H), 1445 cm.$^{-1}$ (CH_2) and 670 cm.$^{-1}$ (CH=CH out of plane). The NMR determined ratio of sp^3 to sp^2 hydrogens was 22.7:1.

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.29; H, 11.60.

Copolymer of 4-vinylcyclohexene and maleic anhydride.- A polymerization bottle was charged with 5.9 g. (55 mmoles) of freshly distilled 4-vinylcyclohexene (b.p. 55°C./63 mm.),

11.9 g. (121 mmole) of recrystallized [illegible]
0.2 g. of recrystallized azoisobutyronitrile [illegible]
of reagent grade benzene. Nitrogen was [illegible]
through the solution for five minutes, [illegible]
sealed and placed in a 50°C. constant [illegible] for
ten days. The polymerization vessel contained [illegible]
and a light yellow solution. The mixture was poured into
one liter of a 50:50 mixture of ethyl ether petroleum ether.
The resulting polymer was filtered off and dried in vacuum
to yield 7.13 g. (42.7 per cent conversion, based on a 2:1,
maleic anhydride: diene copolymer). The copolymer was dis-
solved in dimethylformamide (100 per cent soluble) and
reprecipitated by addition to a stirred 50:50 ether petroleum
ether solution. The polymer had the following properties:
capillary melt temperature greater than 250°C., intrinsic
viscosity of 0.22 in dimethylformamide. The infrared
spectrum of the polymer revealed absorption bands as fol-
lows: 2930 and 2870 cm.$^{-1}$ (C-H), 1865 and 1780 cm.$^{-1}$ (five-
membered ring anhydride) and 1215, 1060 and 910 cm.$^{-1}$. The
NMR determined ratio of sp^3 to sp^2 hydrogen was 23:1.

Partial hydrolysis had occurred during purification.
The limiting analysis for completely hydrolyzed 2:1 co-
polymer would be: Calcd. for $C_{16}H_{20}O_8$: C, 56.46; H, 5.92.

<u>Anal.</u> Calcd. for $C_{16}H_{16}O_6$: C, 63.15; H, [illegible].30.
Found: C, 60.66; H, 5.48.

TABLE 21

PHYSICAL PROPERTIES OF SOLUBLE POLYMERS OF 4-ALLYLCYCLOPENTENE

Polymer number	Capillary melt Temp. (°C.)	Intrinsic viscosity	Vapor pressure molecular weight	Elemental Analysis Calcd. % C	Calcd. % H	Found % C	Found % H
IIc	67	n.d.[1]	N.D.	88.82	11.18	80.86	10.57
IId	157	0.050	1786	88.82	11.18	88.92	11.10
IIf	55	0.175	N.D.	88.82	11.18	88.80	11.14

1 N.D. = not determined

TABLE 22

PHYSICAL PROPERTIES OF SOLUBLE POLYMERS OF 3-ALLYLCYCLOPENTENE

Polymer number	Capillary melt Temp. (°C.)	Intrinsic viscosity	Vapor pressure molecular weight	Elemental Analysis Calcd. % C	% H	Found % C	% H	% O
IVd	180	0.08	3073	88.82	11.18	83.39	10.91	5.57
IVe	174	0.06	7464	88.82	11.18	83.65	10.42	5.62
IVf	120	N.D.[1]	N.D.	88.82	11.18	83.65	10.42	5.62
IVg	102	N.D.	N.D.	88.82	11.18	N.D.	N.D.	N.D.
IVh	112	N.D.	N.D.	88.82	11.18	N.D.	N.D.	N.D.
IVi	129	N.D.	N.D.	88.82	11.18	N.D.	N.D.	N.D.
IVj	19	N.D.	N.D.	88.82	11.18	N.D.	N.D.	N.D.
IVk	59	N.D.	N.D.	88.82	11.18	N.D.	N.D.	N.D.
IVm	63.5	0.02	1471	88.82	11.18	88.73	11.20	N.D.
IVn	58	0.01	1629	88.82	11.18	87.32	11.18	4.38
IVo	64	0.02	1567	88.82	11.18	88.76	11.23	N.D.
IVp	15[illegible]	0.06	2040	88.82	11.18	86.[illegible]	11.12	2.4[illegible]

1 N.D. = not determined

TABLE 23

PHYSICAL PROPERTIES OF SOLUBLE POLYMERS OF 3-ALLYLCYCLOHEXENE

Polymer number	Capillary melt $T_{m.p.}$ (°C.)	Intrinsic viscosity	Vapor pressure molecular weight	Elemental Analysis Calcd. % C	Calcd. % H	Found % C	Found % H
IIIa	167	0.050	2376	88.45	11.55	88.36	11.58
IIIe	155	0.056	3946	88.45	11.55	88.23	11.48
IIIf	75	0.014	1148	88.45	11.55	88.49	11.59
IIIg	80	0.012	1924	88.45	11.55	88.29	11.60

TABLE 24

PHYSICAL PROPERTIES OF SOLUBLE POLYMERS OF 4-ALLYLCYCLOHEXENE

Polymer number	Capillary melt Temp. (°C.)	Intrinsic viscosity	Vapor pressure molecular weight	Elemental Analysis Calcd. % C	Calcd. % H	Found % C	Found % H
Va	67	0.11	N.D.[1]	88.45	11.55	88.56	11.46
Vb	76	0.18	5209	88.45	11.55	88.50	11.47
Vc	115	0.45	>10000	88.45	11.55	88.25	11.60
Vd	110	0.02	2663	88.45	11.55	88.45	11.52

1 N.D. = not determined

TABLE 25

PHYSICAL PROPERTIES OF COPOLYMERS OF DIENES AND MALEIC ANHYDRIDE

Comonomer	Polymer number	Capillary melt (Temp. (°C.)	Intrinsic viscosity	Elemental Analysis Calcd (%)[1] C	H	Found (%) C	H
4-vinylcyclohexene	Ig	235	N.D.[2]	63.15	5.30	62.36	5.70
4-vinylcyclohexene	Ih	-	N.D.	63.15	5.30	N.D.	N.D.
4-vinylcyclohexene	Ii	260	N.D.	63.15	5.30	N.D.	N.D.
4-vinylcyclohexene	Ij	-	N.D.	63.15	5.30	59.14	5.48
hydrolyzed 4-vinylcyclohexene	Ih	300	0.12	56.46	5.92	56.62	5.82
4-vinylcyclohexene	Ik	250	0.22	63.15	5.30	60.65	5.48
3-allylcyclohexene	IIIh	165	N.D.	64.14	5.70	57.33	6.18
3-allylcyclopentene	IVq	≈250	0.17	63.15	5.30	61.58	5.81
4-allylcyclohexene	Vd	177	N.D.	64.14	5.70	51.73	6.20

1 calculated for the 1:2 maleic anhydride, diolefin polymer
2 N.D. = not determined

Synthesis Toward the Preparation of 1,3-Divinylcyclobutane

Dibromopentaerythritol.-A five liter, three-necked flask was equipped with a reflux condenser and a pressure equalizing addition funnel. The flask was charged with 600 g. (4.43 moles) of pentaerythritol, 105 ml. (0.91 moles of 48 per cent hydrobromic acid and 2 liters of glacial acetic acid. The solution was refluxed for an hour and then 1440 ml. (126 moles) 48 per cent HBr was added during a five hour period. The solution was refluxed 2.5 hours and then a final 500 ml. (4.3 moles) of 48 per cent HBr was added over a period of three hours. The solution was refluxed again for 12 hours. The clear brown-orange solution was distilled free of water and acetic acid on a steam bath under a water aspirator induced vacuum. The residual brown liquid was transferred to a two liter, one-neck flask with one liter of absolute ethanol. The flask was treated with 25 ml. of 48 per cent HBR and connected to a 2.5 x 30 cm. glass helices distillation column. The ethyl acetate, ethanol, water azeotrope (b.p. 70°C.) distilled first and then the ethyl acetate, ethanol azeotrope (b.p. 72°C.). An additional 1.1 liters of absolute ethanol was added and the distillation continued until the temperature had reached 77°C. and the odor of ethyl acetate was no longer noticeable. The remaining ethanol was then removed by vacuum distillation. The residual brown oil was treated

with 700 ml. of dry benzene and refluxed over a modified Dean-Stark trap until no more water was given off. The hot benzene solution was transferred into a beaker and set aside to cool and crystallize. The resulting off-white crystals were filtered off, washed with cold benzene and air-dried to yield 649 g. of crude dibromopentaerythritol, m.p. 85°-103°C. The dirty crystals were taken up in two liters of hot water, charcoaled and set aside to cool. Yield: 691.3 g. (60 per cent of theory) of pure white crystals, m.p. 109-111°C. Infrared analysis revealed the following absorption bands: 3305 cm.$^{-1}$ (-OH) and 1036 cm.$^{-1}$ (C-O stretch).

<u>2-Phenyl-5,5-dibromomethyl-1,3-dioxacyclohexane</u>.-To a two liter, one-necked flask was added 846 g. (3.23 moles) of dibromopentaerythritol, 364 g. (3.43 moles) of benzaldehyde, 3.0 g. of p-toluenesulfonic acid and 1.2 liters of dry benzene. The flask was connected to a modified Dean-Stark trap and a reflux condenser. The solution was heated gently to reflux and then refluxed until no water was evolved (about 3 hours, 58 ml. of water collected). After cooling to room temperature, the yellow solution was washed three times (200, 200, 200 ml.) with 5 per cent sodium carbonate and dried over K_2CO_3. The dried solution was stripped of solvent under vacuum to yield a light yellow oil which completely solidified on standing. The solid was

recrystallized from methanol to yield: first crop, 1035 g., m.p. 68-70.5°C., second crop, 44 g., m.p. 68-70°C. Total yield, 1079 g. (95.5 per cent of theory). Infrared analysis revealed the following absorption bands: 1590 cm.$^{-1}$, 1500 cm.$^{-1}$ and 698 cm.$^{-1}$ (phenyl).

Isoamyl 7-phenyl-6,8-dioxospiro(3,5)nonane-2,2-dicarboxylate.-A two liter, three-necked flask was fitted with a combination mechanical stirrer, nitrogen inlet and a reflux condenser (connected to a mercury bubbler). The apparatus was flamed out twice under nitrogen. The flask was charged with one liter of super dry-i-amyl alcohol and 25.3 g. (1.1 moles) of sodium metal. The mixture was stirred overnight, under nitrogen, while heating slightly to achieve complete reaction of the metal. To the light yellow solution of sodium isoamylate was added 240 g. (1.5 moles) of diethyl malonate. The apparatus was fitted for distillation through a 2.5 x 30 cm. glass helices column. The solution was slowly heated until all the ethyl alcohol was removed and the boiling point of isoamyl alcohol was reached (b.p. 127°C., 500 ml. of distillate collected). The reaction solution was cooled slightly, set up for refluxing and then 176 g. (0.5 moles) of 2-phenyl-5,5-dibromomethyl-1,3-dioxacyclohexane was added in one portion. The reaction mixture was refluxed for twenty-two hours with sodium bromide appearing shortly after refluxing commenced. At the end of

the reaction, most of the isoamyl alcohol was removed by distillation at atmospheric pressure. The cooled, reddish brown liquid was treated with water. The emulsion which formed was easily broken by the addition of ethyl ether. The organic layer was separated and the aqueous layer was extracted several times with ether. The ether extracts were combined and dried over K_2CO_3. The residue, after removal of the ether was distilled in two parts: first part, 11.2 g., b.p. 200°C. (2 mm.)-232°C. (1.9 mm.) and 93.8 g., b.p. 232°C. (1.9 mm.)-229°C. (1.2 mm.); second part, 10.9 g., b.p. 200°C. (2 mm.)-226°C. (1.3 mm.) and 65.3 g., b.p. 229.5°C. (1.5 mm.)-227°C. (1 mm.). Both low boiling fractions were dissolved in methanol and recrystallized by cooling in a dry ice-acetone bath. Yield: 11.5 g., m.p. 40-44°C. Total yield of diester, 170.6 g. (79 per cent of theory). Recrystallized diester had a melting point of 41-43°C. Infrared analysis revealed the following absorption bands: 3050 cm.$^{-1}$ (C-OH), 1725 cm.$^{-1}$ (ester), 1595 and 1490 cm.$^{-1}$ (phenyl), 1380 cm.$^{-1}$ (geminal dimethyl), 1270 cm.$^{-1}$ (C-O stretch), and 755 and 695 cm.$^{-1}$ (phenyl).

<u>7-Phenyl-6,8-dioxaspiro(3,5)nonane-2,2-dicarboxylic acid</u>.-To a three liter Erlenmeyer flask fitted with a reflux condenser was added 69.0 g. (1.23 moles) of potassium hydroxide and 1300 ml. of absolute ethanol. The flask was heated on the steam bath until complete solution occurred.

Then 170.9 g. (0.40 moles) of the diisoamyl ester in 500 ml. of absolute ethanol was added in one portion. Almost immediately a white precipitate of the dipotassium salt appeared. The mixture was heated on the steam bath for one-half hour after refluxing commenced. At the end of the reaction period, the flask was cooled in an ice bath for four hours. The resulting white solid was filtered off, washed with cold ethanol and ethyl ether and air dried. Yield: 146 g. of white salt. Concentration of the alcoholic solution yielded an additional 3.6 g. Conversion to the dipotassium salt was quantitative.

The first portion of the dipotassium salt, 146 g., was dissolved in one liter of water, cooled in ice and made acid to Congo Red by addition of 3 N-HCl. The precipitated solid was dissolved in the minimum quantity of ethyl ether and the organic layer was separated. The aqueous layer was extracted twice (200, 200 ml.) with ether, the ether extracts combined, 200 ml. of benzene was added and the ether was boiled off until crystallization began. Yield: 109 g. (96.7 per cent of theory) of crude dicarboxylic acid. Recrystallization yielded pure 7-phenyl-6,8-dioxaspiro(3,5)-nonane-2,2-dicarboxylic acid, m.p. 197-198°C. (m.p. 184-186°C. if heated rapidly). Infrared analysis revealed the following absorption bands: 3500-2800 cm.$^{-1}$ (COOH), 1730 and 1700 cm.$^{-1}$ (COOH), 1595 cm.$^{-1}$ (phenyl) and 752 and 692 cm.$^{-1}$ (phenyl).

<u>1,1,3,3-Cyclobutanetetracarboxylic Acid</u>.-To a 200 ml. round bottom flask fitted with a reflux condenser was added 58.4 g. (0.2 mole) of 7-phenyl-6,8-dioxaspiro(3,5)nonane-2,2-dicarboxylic acid and 50 ml. of 2N-HNO_3. The mixture was heated at reflux for fifteen minutes at which time all of the solid had dissolved and a layer of benzaldehyde was visible. The benzaldehyde layer was separated and the remaining aqueous layer was washed once with a small amount of ether. The aqueous solution was then boiled free of ether on the steam bath.

A one liter, three-necked flask was fitted with a mechanical stirrer, reflux condenser and an addition funnel. The flask was loaded with 200 ml. of concentrated nitric acid and 10 ml. of fuming nitric acid. The apparatus was then heated by an oil bath maintained at 45 to 50°C. The aqueous solution above was placed in the addition funnel and added over ten minutes to the rapidly stirring HNO_3 solution. Copious amounts of nitrogen oxides were evolved. The acid solution was stirred at 50°C. for one hour and then refluxed for three hours. The acidic solution was cooled slightly, moved to a steam bath and distilled nearly to dryness under reduced pressure. A cylindrical, 30 cm. glass tube was used as a distillation column. The apparatus was moved into a hood and 50 ml. of reagent grade formic acid and water was stripped off on the steam bath under

vacuum to leave a yellow-white solid. The solid was taken up in ether, treated with benzene and boiled free of ether until crystallization began. Yield: 33.9 g. (73 per cent of theory) of crude 1,1,3,3-cyclobutanetetracarboxylic acid. Recrystallization from ether-benzene yielded a cream colored solid, m.p. 207.5-208.5°C. (dec.). Infrared analysis revealed the following absorption bands: 3600-2800 cm.$^{-1}$ (COOH), 3450 cm.$^{-1}$ (COOH), 1710 cm.$^{-1}$ (COOH), 1405, 1280 and 905 cm.$^{-1}$ (COOH).

<u>Cis-1,3-cyclobutanedicarboxylic acid and trans-1,3-cyclobutanedicarboxylic acid</u>.-To a 200 ml., round-bottomed flask fitted with a reflux condenser and drying tube was added 50 g. (0.216 moles) of 1,1,3,3-cyclobutanetetracarboxylic acid. The flask was heated for 19 minutes in an oil bath maintained at about 220°C. The brown liquid solidified on cooling to room temperature. The brown solid was treated with 70 g. of acetyl chloride and then refluxed for 2.5 hours. After cooling slightly, the brown liquid was transferred to a 100 ml. round-bottomed flask and freed of volatile materials by distillation on a steam bath under vacuum. The thick brown-black liquid was further freed of volatiles by heating with an oil bath (120-130°C.) under high vacuum. When the anhydride began to sublime, the distillation apparatus was replaced by a straight tube, 2.5 x 30 cm., and connected to the vacuum system. The

anhydride began to sublime slowly at 1 mm. The straight tube must be scraped free of crystalline anhydride at frequent intervals. The crude anhydride was resublimed in the same manner to yield pure white cis-1,3-cyclobutanedicarboxylic anhydride, 12.3 g. (45 per cent), m.p. 128-133°C. Infrared analysis revealed the following absorption bands: 1760 and 1725 cm.$^{-1}$ (acid anhydride) and many strong bands 900 to 1300 cm.$^{-1}$.

The cis anhydride was converted into cis-1,3-cyclobutanedicarboxylic acid by refluxing with an equal weight of 6N-HCl for ten minutes. Removal of the hydrochloric acid on a steam bath and recrystallization from acetone-benzene yielded white needles, m.p. 132.5-133.5°C. Infrared analysis revealed the following absorptions: 3200-2500 cm.$^{-1}$ (COOH), 1720 cm.$^{-1}$, 1430 cm.$^{-1}$ and 920 cm.$^{-1}$ (COOH).

<u>Anal</u>. Calcd. for $C_6H_8O_4$: C, 50.00; H, 5.60. Found: C, 50.02; H, 5.68.

trans-1,3-Cyclobutanedicarboxylic acid was isolated from the residue remaining after the distillation of the cis-anhydride. The black residue was refluxed a few minutes with 6N-HCl and then evaporated to dryness under vacuum. The remaining brown-black solid was placed in a suitable sized beaker and heated on a hot plate to boiling with 100 ml. portions of xylene. This treatment was continued until little or no soluble material crystallized after decantation.

Total yield of crude trans-acid was 15.7 g. (50 per cent). The crude trans-acid was freed of the cis-acid impurity by recrystallization from 6N-HCl to yield white needles, m.p. 190-191°C. Infrared analysis revealed the following absorptions: 3200-2500 cm.$^{-1}$ (COOH), 1700 cm.$^{-1}$, 1425 cm.$^{-1}$ and 930 cm.$^{-1}$ (COOH).

Anal. Calcd. for $C_6H_8O_4$: C, 50.00; H, 5.60. Found: C, 50.14; H, 5.70.

cis and trans Ethyl 1,3-cyclobutanedicarboxylate.-The diethyl esters were prepared according to the general procedure of Nateleon and Gottfried (204). The cis-diethyl ester was prepared from the anhydride while the trans-diethyl ester was made from the trans-diacid. 5.38 g. (42.7 moles) of the anhydride, 8.1 g. (175 moles) of absolute ethyl alcohol, 3 drops of concentrated H_2SO_4 and 100 ml. of benzene were refluxed over 5 g. of anhydrous $MgSO_4$ in a soxhlet extractor for 24 hours. After 12 hours, the $MgSO_4$ was replenished and an additional 2 ml. of alcohol was added. The resulting yellow solution was cooled, washed with water, 5 per cent $NaHCO_3$ and water. After drying over $MgSO_4$, distillation through a 1.5 x 12 cm. Vigreux column yielded pure diethyl cis-1,3-cyclobutanedicarboxylate, 7.8 g. (92 per cent of theory), b.p. 116-117.5°C. (7.5 mm.), n_D^{21} 1.4414. Infrared analysis revealed the following absorption bands: 1735, 1200 and 1050 cm.$^{-1}$.

The corresponding cis-dimethyl ester had a boiling point of 128-129°C. (23 mm.), n_D^{21} 1.4462.

The trans-diethyl ester was prepared by an analogous procedure to yield pure product, b.p. 73°C. (0.1 mm.), n_D^{22} 1.4401 in 86 per cent yield. Infrared analysis revealed the following absorption bands: 1733, 1200 and 1050 cm.$^{-1}$.

cis and trans-1,3-Cyclobutanedicarboxaldehyde.-The dialdehydes were prepared by the general procedure of Zakharkin et al. (166). A 100 ml. three-necked flask was equipped with a mechanical stirrer, addition funnel, reflux condenser, alcohol thermometer and a nitrogen bubbler. After flame drying, the flask was loaded with 12 g. (60 moles) of the diethyl ester in 24 ml. of dry tetrahydrofuran (THF). The addition funnel was charged with a slurry of 1.8 g. (33 mmoles) of sodiumaluminumhydride in 30 ml. of dry THF. The slurry was added over 1.5 hours to the diester solution maintained as closely as possible at -50°C. for 6-7 hours and then decomposed by pouring into an equivalent amount of 3N-HCl and ice. The solution was treated with ethyl ether and extracted six times (200 ml. total volumn), dried over $MgSO_4$ and distilled. Distillation gave 1.8 g. (27 per cent) of a fraction boiling at 76-79°C. (1 mm.), n_D^{20} 1.4519 in the case of the cis-dialdehyde. A similar procedure produced the trans-dialdehyde, b.p. 67.5-71°C. (0.7 mm.) n_D^{20} 1.4510 in 61 per cent yield. Distille-

tion of the cis-aldehyde must be accomplished rapidly and at as low a temperature as possible since much material does not distill and is presumably the polyaldehyde. The trans-dialdehyde does not polymerize under the distillation conditions. The NMR spectra of both dialdehyde fractions revealed the presence of ethyl ester to aldehyde groups in the ratio of 3:1. Both dialdehydes form exceedingly insoluble di-DNP's with 2,4-dinitrophenylhydrazine. The cis-dialdehyde gave a yellow di-DNP sparingly soluble in dioxane with a m.p. of 240-242°C.

Anal. Calcd. for $C_{18}H_{16}N_8O_8$: C, 45.57; H, 3.82. Found: C, 45.58; H, 3.91.

The trans-dialdehyde distillation fraction contained mainly the monoaldehyde, monoester. This product was characterized by its mono-DNP which was easily recrystallized from 95 per cent ethanol as shiny yellow needles, m.p. 111-113°C., with a phase change also at 101-103°C. Infrared analysis revealed the following absorption bands: 1725, 1200 and 1050 cm.$^{-1}$ (ester), 1630 cm.$^{-1}$ (C=N), 1580 and 1340 cm.$^{-1}$ (nitro) and 1530 cm.$^{-1}$ (aromatic).

Anal. Calcd. for $C_{14}H_{16}N_4O_6$: C, 50.00; H, 4.80; N, 16.66. Found: C, 49.81; H, 4.71; N, 16.50.

The presence of unreacted ester groupings in the dialdehyde fraction indicates the reaction did not go to completion. It is suggested that the reaction time be

extended from the usual 5-7 hours to possible 12 hours or longer, as necessary.

Due to their limited quantities, the distillations on the aldehyde fractions were the simple bulb to bulb type. It is suggested that the reaction be run on a larger scale so an efficient column can be used. The cis-aldehyde must be distilled at as low a temperature as possible since thermal polymerization greatly decreases the yield.

The reduction of the trans-diester appears to give only monoaldehyde. If increasing the reaction time or $NaAlH_4$ concentration does not yield the dialdehyde, another reaction scheme should be applied. For example, reduction of the trans-dianilide with $LiAlH_4$ (205).

SUMMARY

3-Allylcyclopentene, 4-allylcyclopentene, 3-allylcyclohexene and 4-allylcyclohexene have been prepared by the Grignard coupling reaction of the appropriate unsaturated halide and an allyl halide. The attempted synthesis of 1,3-divinylcyclobutane was reported.

The far ultraviolet spectra of the allylcycloalkenes and 4-vinylcyclohexene generally absorbed hypsochromically relative to cyclohexene and 3-propylcyclohexene. This was interpreted by a destabilizing effect of the double bonds on each other. The spectrum of 1,4-dimethylenecyclohexane exhibited two long wavelength shoulders which were interpreted as possibly arising from an energy stabilizing interaction between the double bonds.

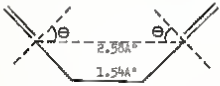
The allylcycloalkenes were polymerized by both metal alkyl coordination catalyst and cationic initiators. The polymers derived from these monomers invariably contained polymeric fractions (27-99 per cent) which were soluble in nonpolar organic solvents. Calculations based on NMR spectral data indicated the cationic polymers were 68-95 per cent cyclized. The per cent cyclization was found to parallel the interolefinic separation in the monomer. Coordination polymerization yielded somewhat lower per cent

cyclizations (54-80 per cent) in all cases except for 4-allylcyclohexene. 4-Allylcyclohexene gave only 5-54 per cent cyclization.

4-Vinylcyclohexene, 3-allylcyclopentene and 3-allylcyclohexene produced soluble copolymers with maleic anhydride. Elemental analysis indicated that there were two maleic anhydride units for each monomer molecule polymerized. A cyclicopolymerization mechanism suggested the formation of a multicyclic repeating unit. The other monomers gave crosslinked polymers since maleic anhydride could not be incorporated into a six-membered ring.

APPENDIX

HMO CALCULATIONS FOR 1,4-DIMETHYLENECYCLOHEXANE



$\theta = 19°52$

Using the procedure outlined in reference (169).

I. Calculation of S_{12}

$$S_{12} = S_{\sigma\sigma} \cos \theta_1, \cos \theta_2 + S_{\pi\pi} \sin \theta_1, \theta_2$$

extrapolating Kopineck's data (170) at

2.58 A°: $S_{\sigma\sigma} = 0.128$

$S_{\pi\pi} = 0.026$

$$S_{12} = 0.128\ (0.940)^2 + 0.026(0.340)^2 = 0.116$$

II. Calculation of β'

$$\beta' = \beta \frac{S_{12}/(1 + S_{12})}{S/(1 + S)} \qquad S(CH_2{=}CH_2) = 0.28$$

$$\beta' = \frac{0.116/(1\ \ 0.116)}{0.28/(1\ \ 0.28)} = 0.48$$

III. Calculation of Energy

$$\begin{vmatrix} X & 1 & 0 & 0 \\ 1 & X & .48 & 0 \\ 0 & .48 & X & 1 \\ 0 & 0 & 1 & X \end{vmatrix} = 0 \qquad X = \frac{\alpha - E}{\beta}$$

$$x^4 - 2.23x^2 + 1 = 0$$

$$x = 1.269 \text{ and } 0.7874$$

$$E = \pm 1.269 \ , \ \pm 0.787$$

IV. Delocalization Energy (D.E.)

E of $= 4\alpha + 4.112\ \beta$

$- E$ of $2(C{=}C)$ $= 4\alpha + 4\ \beta$

D.E. $= 0.112\ \beta$

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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